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Supporting Information

Phosphine-Catalyzed Domino Reaction: A Novel Sequential [2 +3] and [3 + 2] Annulation Reaction of γ-Substituent Allenoates to Construct Bicyclic[3, 3, 0]octene Derivatives

Erqing Li,[a] You Huang*[a]

State Key Laboratory and Institute of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering(Tianjin), *Nankai University, Tianjin 300071, China*.

hyou@nankai.edu.cn

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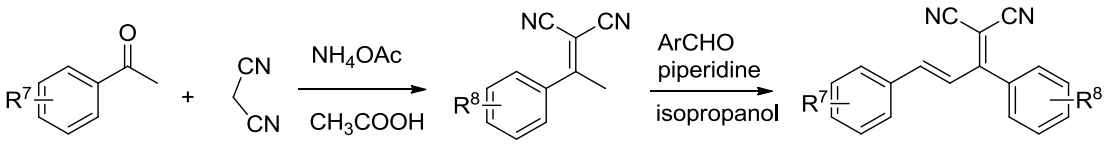
I. General Information

All the solvents were used without further purification. The ^{1}H NMR and spectra was recorded at 400MHz, ^{13}C NMR was recorded at 100MHz.^{1}H and ^{13}C NMR Chemical shifts were calibrated to tetramethylsilane as an external reference. Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet: t, triplet; q, quartet; m, multiplet; HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected.

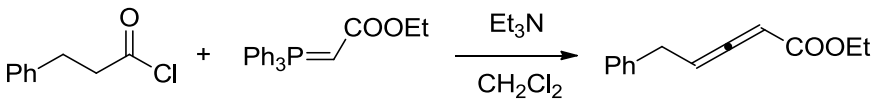
II. General procedure for the (*E*)-2-(1,3-diarylallyli-dene)malononitrile 1.



Malononitrile (32 mmol) and the ketone (28 mmol) were dissolved in 20 mL of toluene containing ammonium acetate (500 mg, 6.5 mmol) and glacial acetic acid (2 mL) in a 50 ml flask. By refluxing vigorously, the water formed in the reaction was removed by a Dean and Stark trap placed under the reflux condenser. Evaporation of the toluene left a residue.[1]

2-(1-Phenylethylidene)malononitrile (0.334 g, 2.14 mmol), aldehydes (2.35 mmol), piperidine 0.214 mmol) were stirred in 2-propanol (2 mL) at 343 K for 24 h. Then the reaction was cooled to room temperature, and the solution was filtered to obtain a yellow solid. Recrystallization from hot ethanol afforded the pure compound **1**.[2]

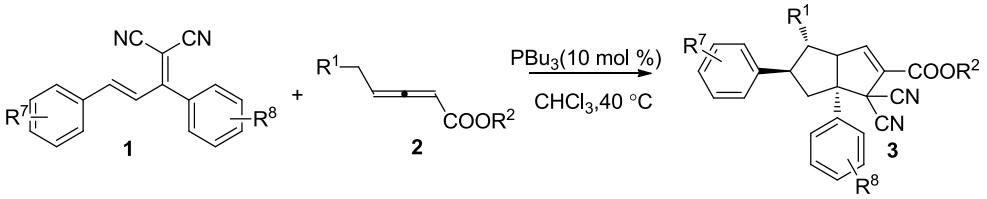
III. Synthesis of 5-Phenyl-penta-2,3-dienoic acid ethyl ester 2.



Allenoate **2** is a known compound and synthesized according to a similar method developed by Hansen.[3] To a solution of (ethoxycarbonylmethylene)-triphenylphosphorane (0.1 mol,) in dichloromethane (400 mL) was added 1.1 equivalent of triethylamine (0.11 mol,). After stirred for about 15 minutes, 1.1 equivalent of 3-phenylpropanoyl chloride (0.11 mol,) was added dropwise.

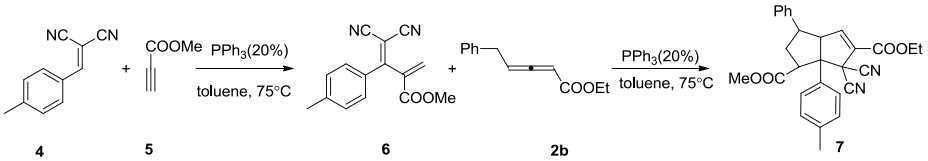
Then the reaction mixture was allowed to be warmed up to room temperature and stirred overnight. The resulting mixture was carefully evaporated to remove most of the solvent, and the residue was extracted by petroleum ether (b.p. 30 - 60 ºC, 5 × 100 mL). The combined extracting was concentrated and the residue was subjected to column chromatography (eluant: 5% EtOAc in petroleum ether) to provide the allenoate 1 as yellow oil.[4]

IV. General procedure for the synthesis of [3.3.0]bicyclic derivatives 3.



To a dry flask filled with nitrogen were added **1** (0.3 mmol) and **2** (0.4 mmol) in 2 mL $CHCl_3$ under N_2 atmosphere. PBu_3 (0.06 mmol) was added. This solution was stirred at 40 °C until the complete consumption of the starting material as monitored by TLC. After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60 - 120 mesh)column using 10:1 petroleum ether –ethyl acetate solvent mixture as eluent to afford **3.**

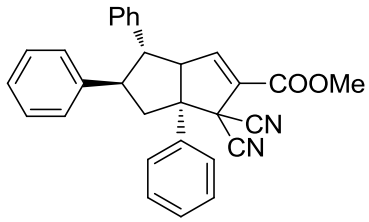
V. General procedure for a pot synthesis of [3.3.0]bicyclic derivatives 7.



To a dry flask filled were added **4** (0.3 mmol) and PPh_3 (0.06 mmol) in 7 mL Toluene under N_2 atmosphere. And **5** in 3 mL Toluene (0.6 mmol) was dropwised slowly over 2h. This solution was stirred at 75 °C until the complete consumption of the starting material as monitored by TLC. **2b** (0.6 mmol) and PPh_3 (0.06 mmol) were added under the same temperature. After the complete consumption of the starting material as monitored by TLC, the removal of the solvent. And the residue was subjected to chromatography on a silica gel (60 - 120 mesh)column using 10:1 petroleum ether –ethyl acetate solvent mixture as eluent to afford **7.**

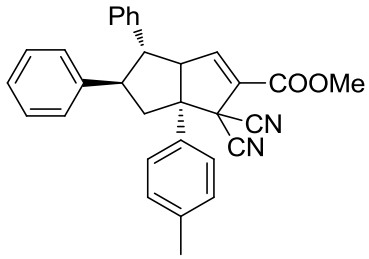
VI. Analytical Data for Compounds.

methyl 1,1-dicyano-4,5,6a-triphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3a.



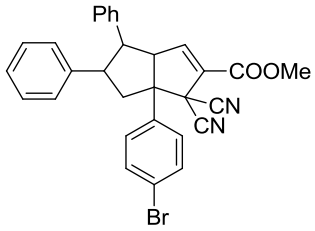
white solid. mp: 87-88°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.56 (t, J = 7.5 Hz, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.36 (d, J = 1.8 Hz, 1H), 7.27 (t, J = 7.2 Hz, 2H), 7.24 – 7.21 (m, 1H), 7.15 (t, J = 7.8 Hz, 3H), 7.08 (d, J = 7.5 Hz, 2H), 7.00 (d, J = 7.3 Hz, 2H), 4.22 (d, J = 2.3 Hz, 1H), 3.91 (s, 3H), 3.23 (d, J = 4.8 Hz, 2H), 3.11 – 3.02 (m, 1H), 2.71 – 2.58 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 153.2, 141.0, 139.4, 138.5, 129.7, 129.4, 129.1, 128.6, 127.5, 127.4, 127.2, 127.1, 113.2, 112.9, 77.5, 77.1, 76.8, 65.4, 60.4, 57.0, 53.0, 50.6, 50.2, 46.2 ppm; IR (KBr): ῡ = 3061, 3030, 2955, 1727, 1642, 1265, 742, 700 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{30}H_{24}O_2N_2Na^+$ 467.1730, found 467.1731.

methyl 1,1-dicyano-4,5-diphenyl-6a-(p-tolyl)-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3b.



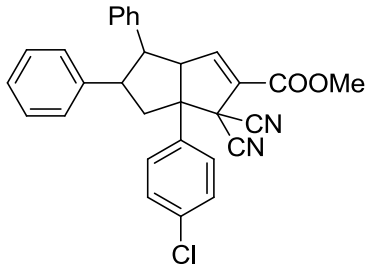
White solid; mp: 196-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 2H), 7.45 – 7.40 (m, 3H), 7.36 – 7.28 (m, 3H), 7.27 – 7.19 (m, 3H), 7.15 (d, *J* = 7.0 Hz, 2H), 7.06 (d, *J* = 6.5 Hz, 2H), 4.25 (t, *J* = 12.3 Hz, 1H), 3.98 (s, 3H), 3.34 – 3.25 (m, 2H), 3.19 – 3.07 (m, 1H), 2.76 – 2.67 (m, 1H), 2.50 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 153.3, 141.1, 139.5, 139.2, 135.4, 130.3, 129.0, 128.6, 127.6, 127.4, 127.4, 127.2, 127.1, 127.0, 113.3, 113.0, 77.5, 77.2, 76.8, 65.2, 60.5, 57.1, 53.0, 50.7, 50.3, 46.1, 21.2 ppm; IR (KBr): ῡ = 3061, 3030, 2954, 1726, 1642, 1264, 738, 700 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{31}H_{26}O_2N_2Na^+$ 481.1886, found 481.1885.

methyl 6a-(4-bromophenyl)-1,1-dicyano-4,5-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3c.



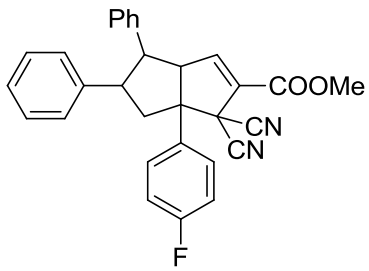
White solid; mp: 124-125 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.58 (s, 2H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.35 – 7.26 (m, 3H), 7.26 – 7.18 (m, 3H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 7.4 Hz, 2H), 4.19 (d, *J* = 3.9 Hz, 1H), 3.98 (s, 3H), 3.27 (qd, *J* = 11.2, 5.2 Hz, 2H), 3.08 – 2.98 (m, 1H), 2.71 (q, *J* = 11.9 Hz, 1H)ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 152.9, 140.7, 139.1, 137.5, 132.8, 129.1, 128.8, 128.7, 127.5, 127.4, 127.3, 127.0, 123.7, 112.9, 112.7, 77.5, 77.2, 76.8, 65.1, 60.6, 56.9, 53.1, 50.3, 50.1, 46.0 ppm; IR (KBr): ῡ = 3061, 3030, 2955, 1728, 1644, 1266, 741, 701 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{30}H_{23}O_2N_2BrNa^+$ 545.0835, found 545.0834.

methyl 6a-(4-chlorophenyl)-1,1-dicyano-4,5-diphenyl-1,3a,4,5,6,6a-hexahydro-pentalene-2-carboxylate 3d.



White solid, mp: 205-206 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 9.4 Hz, 1H), 7.29 – 7.20 (m, 3H), 7.20 – 7.12 (m, 3H), 7.05 (t, *J* = 10.3 Hz, 2H), 7.00 (d, *J* = 7.1 Hz, 2H), 4.13 (t, *J* = 11.2 Hz, 1H), 3.91 (s, 3H), 3.29 – 3.14 (m, 2H), 3.00 (dd, *J* = 12.2, 3.4 Hz, 1H), 2.65 (t, *J* = 12.5 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 152.9, 140.8, 139.1, 137.0, 135.5, 130.0, 129.1, 128.7, 128.6, 127.5, 127.4, 127.4, 127.3, 127.1, 113.0, 112.8, 77.5, 77.1, 76.8, 65.0, 60.7, 56.9, 53.1, 50.4, 50.1, 46.1 ppm; IR (KBr): ῡ = 2964, 1736, 1720, 1639, 736, 705 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{30}H_{23}O_2N_2ClNa^+$ 501.1340, found 501.1343.

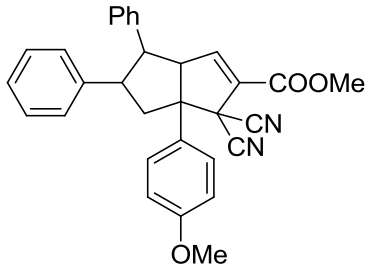
methyl 1,1-dicyano-6a-(4-fluorophenyl)-4,5-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3e.



White solid; mp: 205-206 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.30 – 7.21 (m, 5H), 7.16 (dd, *J* = 8.7, 6.9 Hz, 3H), 7.06 (d, *J* = 7.0 Hz, 2H), 7.00 (d, *J* = 6.5 Hz, 2H),

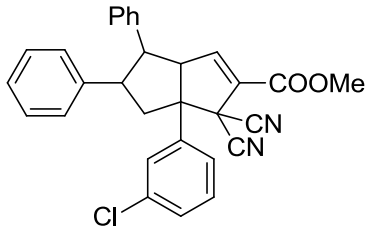
4.16 (d, *J* = 3.6 Hz, 1H), 3.91 (s, 3H), 3.23 (qd, *J* = 11.2, 5.2 Hz, 2H), 3.02 (dd, *J* = 12.0, 3.6 Hz, 1H), 2.64 (dd, *J* = 22.6, 10.1 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 161.8, 161.2, 153.0, 140.9, 139.2, 134.3, 129.1, 128.7, 127.5, 127.5, 127.4, 127.3, 127.1, 113.1, 112.8, 77.5, 77.2, 76.8, 65.0, 60.9, 56.9, 53.0, 50.6, 50.2, 46.1 ppm; IR (KBr): ῡ = 3077, 3030, 2955, 1728, 1644, 1265,742, 701 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{30}H_{23}O_2N_2FNa^+$ 485.1636, found 485.1635.

methyl 1,1-dicyano-6a-(4-methoxyphenyl)-4,5-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3f.



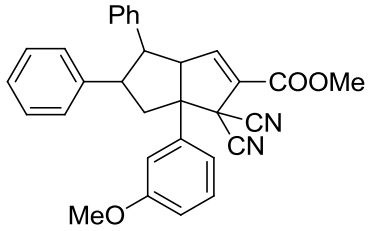
White solid; mp: 215-216 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 2H), 7.34 (s, 1H), 7.26 (t, *J* = 6.6 Hz, 2H), 7.23 – 7.18 (m, 1H), 7.20 – 7.11 (m, 3H), 7.05 (d, *J* = 7.8 Hz, 4H), 6.99 (t, *J* = 8.1 Hz, 2H), 4.14 (d, *J* = 19.9 Hz, 1H), 3.90 (s, 3H), 3.85 (s, 3H), 3.28 – 3.16 (m, 2H), 3.04 (d, *J* = 12.3 Hz, 1H), 2.70 – 2.52 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 160.1, 153.3, 141.2, 139.5, 130.1, 129.1, 128.6, 128.4, 127.6, 127.4, 127.4, 127.2, 127.1, 113.3, 113.0, 77.5, 77.2, 76.9, 65.0, 60.8, 57.1, 55.4, 52.9, 50.8, 50.4, 46.0 ppm; IR (KBr): ῡ = 3062, 3030, 2955, 1726, 1642, 1254,739, 701 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{31}H_{26}O_3N_2Na^+$ 497.1836, found 497.1836.

methyl 6a-(3-chlorophenyl)-1,1-dicyano-4,5-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3g.



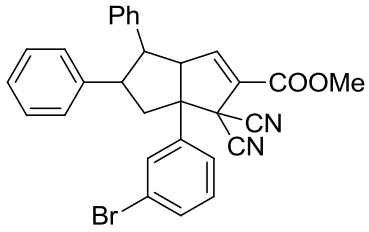
White solid; mp: 220-221 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 2H), 7.48 (dd, *J* = 10.8, 4.6 Hz, 2H), 7.35 (d, *J* = 2.3 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 5.0 Hz, 1H), 7.21 – 7.13 (m, 3H), 7.07 (t, *J* = 7.5 Hz, 2H), 7.04 – 6.98 (m, 2H), 4.13 (t, *J* = 8.3 Hz, 1H), 3.92 (s, 3H), 3.29 – 3.18 (m, 2H), 3.00 (dd, *J* = 18.8, 8.3 Hz, 1H), 2.70 – 2.59 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 152.8, 140.6, 139.0, 130.9, 129.6, 129.2, 128.6, 127.5, 127.4, 127.3, 127.1, 125.5, 112.9, 112.7, 77.4, 77.1, 76.8, 65.1, 60.7, 56.9, 53.0, 50.3, 50.0, 46.1 ppm; IR (KBr): ῡ = 3062, 3030, 2955, 1726, 1642, 1252,739, 701 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{30}H_{23}O_2N_2ClNa^+$ 501.1340, found 501.1341.

methyl 1,1-dicyano-6a-(3-methoxyphenyl)-4,5-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3h.



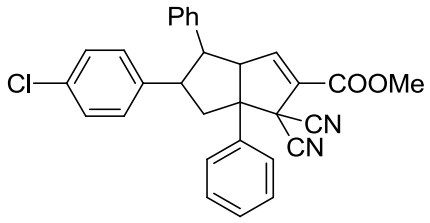
White solid; mp: 86-87 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 2.3 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.19 – 7.15 (m, 3H), 7.12 (d, *J* = 7.1 Hz, 2H), 7.04 – 6.98 (m, 3H), 4.18 (d, *J* = 2.7 Hz, 1H), 3.88 (s, 1H), 3.84 (s, 3H), 3.32 – 3.19 (m, 2H), 3.08 – 2.98 (m, 1H), 2.70 – 2.54 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.22, 153.14, 141.01, 140.13, 139.39, 129.05, 128.58, 127.56, 127.39, 127.18, 127.10, 113.24, 112.83, 77.45, 77.14, 76.82, 65.41, 60.41, 56.84, 55.36, 52.97, 50.51, 50.04, 46.3 ppm; IR (KBr): ῡ = 3062, 3030, 2955, 1726, 1642, 1265,737, 700 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{31}H_{26}O_3N_2Na^+$ 497.1836, found 497.1839.

methyl 6a-(3-bromophenyl)-1,1-dicyano-4,5-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3i.



White solid; mp: 214-215 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 2.1 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.24 (dd, *J* = 8.0, 6.4 Hz, 1H), 7.22 – 7.14 (m, 3H), 7.09 (d, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 6.4 Hz, 2H), 4.13 (d, *J* = 10.3 Hz, 1H), 3.93 (s, 3H), 3.30 – 3.15 (m, 2H), 3.06 – 2.93 (m, 1H), 2.72 – 2.57 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 152.7, 140.9, 140.6, 139.0, 132.5, 129.2, 128.6, 127.5, 127.4, 127.3, 127.0, 112.9, 112.6, 77.4, 77.1, 76.8, 65.1, 60.7, 56.9, 53.0, 50.3, 49.9, 46.1 ppm; IR (KBr): ῡ = 3063, 3030, 2954, 1726, 1643, 1265,738, 700 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{30}H_{23}O_2N_2BrNa^+$ 545.0835, found 545.0832.

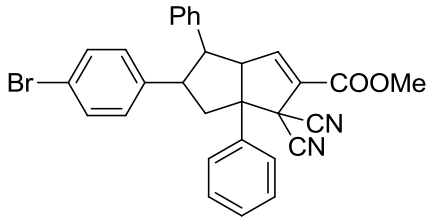
methyl 5-(4-chlorophenyl)-1,1-dicyano-4,6a-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3j.



White solid; mp: 186-187 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 2H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.53 – 7.46 (m, 1H), 7.34 (d, *J* = 2.2 Hz, 1H), 7.30 – 7.20 (m, 3H), 7.11 (t, *J* = 8.0 Hz, 2H), 7.10 – 7.03 (m, 2H), 6.91 (dd, *J* = 8.4, 1.9 Hz, 2H), 4.22 (s, 1H), 3.91 (d, *J* = 5.7 Hz, 3H), 3.30 – 3.12 (m, 2H), 3.05 (d, *J* = 11.2 Hz, 1H), 2.70 – 2.53 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 152.9, 140.6, 138.4, 137.9, 132.9, 129.7, 129.4, 129.2, 128.7, 128.6, 128.5, 127.6, 127.5, 127.1, 113.2, 112.8, 77.5, 77.2, 76.9, 65.4, 60.3, 57.2, 53.0, 50.6, 49.7, 45.9 ppm; IR (KBr): ῡ = 3062, 3030, 2954, 1727, 1643,

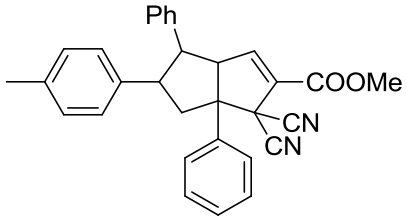
1264,739, 700 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{30}H_{23}O_2N_2ClNa^+$ 501.1340, found 501.1339.

methyl 5-(4-bromophenyl)-1,1-dicyano-4,6a-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3k.



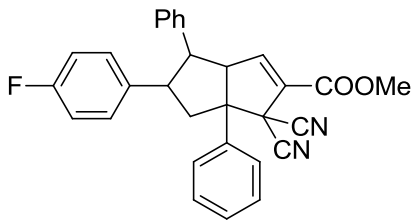
White solid; mp: 187-188 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.56 (t, *J* = 7.5 Hz, 3H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 5.1 Hz, 1H), 7.31 – 7.18 (m, 7H), 7.06 (d, *J* = 7.3 Hz, 3H), 6.85 (d, *J* = 8.3 Hz, 3H), 4.36 – 4.11 (m, 1H), 3.91 (s, 4H), 3.25 – 3.10 (m, 3H), 3.08 – 2.99 (m, 1H), 2.63 (d, *J* = 12.4 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 152.9, 140.5, 138.4, 138.3, 131.7, 129.7, 129.4, 129.2, 128.8, 127.6, 127.5, 127.1, 121.0, 113.2, 112.8, 77.5, 77.2, 76.8, 65.4, 60.3, 57.2, 53.0, 50.6, 49.8, 45.8 ppm; IR (KBr): ῡ = 3062, 3030, 2954, 1727, 1643, 1264,739, 700 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{30}H_{23}O_2N_2BrNa^+$ 545.0835, found 545.0838.

methyl 1,1-dicyano-4,6a-diphenyl-5-(p-tolyl)-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3l.



White solid; mp: 95-96 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.51 – 7.44 (m, 1H), 7.35 (s, 1H), 7.30 – 7.23 (m, 2H), 7.21 (dd, *J* = 8.6, 4.5 Hz, 1H), 7.07 (t, *J* = 11.2 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 7.7 Hz, 2H), 4.20 (s, 1H), 3.91 (s, 3H), 3.35 – 3.10 (m, 2H), 3.03 (d, *J* = 12.0 Hz, 1H), 2.63 (t, *J* = 10.3 Hz, 1H), 2.23 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 153.2, 141.1, 138.6, 136.8, 136.3, 129.6, 129.3, 129.3, 129.0, 127.6, 127.4, 127.3, 127.1, 127.0, 113.2, 112.9, 77.4, 77.1, 76.8, 65.4, 60.4, 57.0, 53.0, 50.6, 49.8, 46.3, 21.0 ppm; IR (KBr): ῡ = 3060, 3029, 2954, 1727, 1642, 1264,744, 702 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{31}H_{26}O_2N_2Na^+$ 481.1886, found 481.2007.

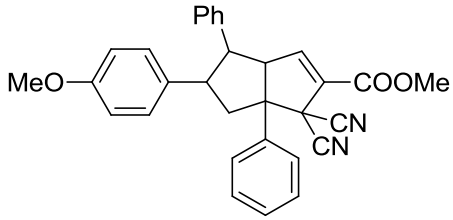
methyl 1,1-dicyano-5-(4-fluorophenyl)-4,6a-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3m.



White solid; mp: 229-230 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 2H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 6.6 Hz, 1H), 7.32 – 7.21 (m, 3H), 7.07 (d, *J* = 7.4 Hz, 2H), 6.95 (dd,

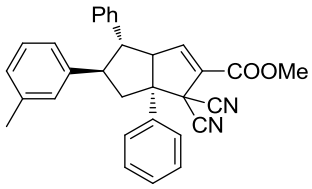
J = 8.1, 5.7 Hz, 2H), 6.86 (t, *J* = 8.6 Hz, 2H), 4.22 (d, *J* = 5.0 Hz, 1H), 3.93 (s, 2H), 3.26 – 3.17 (m, 1H), 3.15 (dd, *J* = 11.0, 6.0 Hz, 1H), 3.06 (dd, *J* = 12.3, 4.2 Hz, 1H), 2.62 (t, *J* = 12.3 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 161.2, 160.6, 153.0, 140.7, 138.4, 135.0, 129.9, 129.4, 129.1, 128.6, 128.5, 127.5, 127.4, 127.1, 115.5, 115.3, 113.2, 112.8, 77.4, 77.1, 76.8, 65.3, 60.3, 57.4, 53.0, 50.6, 49.6, 46.0 ppm; IR (KBr): ῡ = 3062, 3031, 2955, 1726, 1643, 1263,740, 702 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{30}H_{23}O_2N_2FNa^+$ 485.1636, found 485.1637.

methyl 1,1-dicyano-5-(4-methoxyphenyl)-4,6a-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3n.



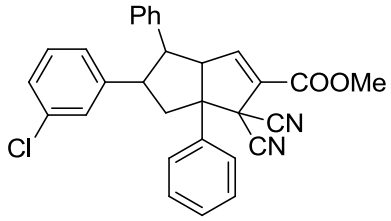
White solid; mp: 97-98 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.33 (d, *J* = 21.1 Hz, 1H), 7.25 (td, *J* = 14.2, 6.9 Hz, 3H), 7.08 (d, *J* = 7.2 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 4.21 (s, 1H), 3.92 (s, 3H), 3.70 (s, 3H), 3.18 (d, *J* = 4.6 Hz, 2H), 3.05 (t, *J* = 13.1 Hz, 1H), 2.62 (dt, *J* = 19.6, 6.0 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 158.6, 153.2, 141.1, 138.6, 131.3, 129.3, 129.1, 128.0, 127.6, 127.4, 127.1, 113.9, 113.2, 112.9, 77.4, 77.1, 76.8, 65.3, 60.3, 57.2, 55.2, 53.0, 50.6, 49.5, 46.3 ppm; IR (KBr): ῡ = 3061, 3030, 2955, 1726, 1643, 1249,741, 702 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{31}H_{26}O_3N_2Na^+$ 497.1836, found 497.1973.

methyl 1,1-dicyano-4,6a-diphenyl-5-(m-tolyl)-1,3a,4,5,6,6a-hexahydropentalene-2- carboxylate 3o.



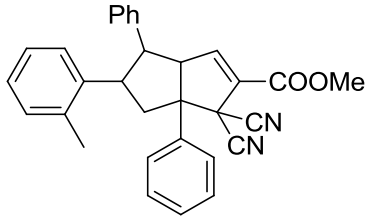
White solid. mp: 174-175°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.37 (s, 1H), 7.37 (s, 1H), 7.30 – 7.24 (m, 2H), 7.24 – 7.18 (m, 1H), 7.12 – 7.06 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.4 Hz, 1H), 6.83 (s, 1H), 6.77 (d, *J* = 7.3 Hz, 1H), 4.21 (d, *J* = 4.0 Hz, 1H), 3.91 (s, 3H), 3.30 – 3.16 (m, 2H), 3.04 (dd, *J* = 12.3, 3.1 Hz, 1H), 2.63 (t, *J* = 12.4 Hz, 1H), 2.22 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 153.3, 141.1, 139.3, 138.5, 138.2, 129.7, 129.3, 129.1, 128.5, 128.0, 127.7, 127.5, 127.4, 127.1, 124.3, 113.2, 112.9, 77.5, 77.1, 76.8, 65.4, 60.4, 56.8, 53.0, 50.6, 50.1, 46.4, 21.4 ppm; IR (KBr): ῡ = 3061, 3030, 2954, 1727, 1643, 1263, 744, 700 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{31}H_{26}O_2N_2Na^+$ 481.1886, found 481.1895.

methyl 5-(3-chlorophenyl)-1,1-dicyano-4,6a-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3p.



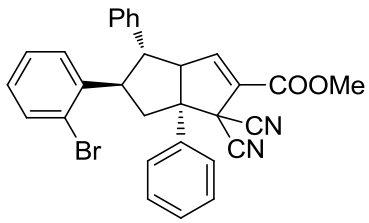
White solid. mp: 194-195°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.56 (dd, *J* = 16.0, 8.3 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.34 (t, *J* = 8.1 Hz, 1H), 7.32 – 7.21 (m, 3H), 7.17 – 7.05 (m, 4H), 7.01 (s, 1H), 6.85 (d, *J* = 7.2 Hz, 1H), 4.31 – 4.11 (m, 1H), 3.93 (s, 3H), 3.30 – 3.15 (m, 2H), 3.13 – 2.96 (m, 1H), 2.67 – 2.52 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 152.8, 141.5, 140.5, 138.2, 134.4, 129.8, 129.5, 129.2, 127.6, 127.4, 127.4, 127.1, 127.1, 125.4, 113.1, 112.7, 77.5, 77.2, 76.8, 65.4, 60.2, 56.9, 53.0, 50.6, 49.9, 46.0 ppm; IR (KBr): ῡ = 3062, 3030, 2955, 1726, 1642, 1252, 739, 701 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{30}H_{23}O_2N_2ClNa^{+}$ 501.1340, found 501.1341.

methyl 1,1-dicyano-4,6a-diphenyl-5-(o-tolyl)-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3q.



White solid. mp: 89-90°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 6.4 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.54 – 7.45 (m, 1H), 7.37 (d, *J* = 16.5 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.26 – 7.09 (m, 4H), 7.02 (dd, *J* = 14.6, 7.3 Hz, 2H), 7.00 – 6.91 (m, 1H), 4.27 (d, *J* = 3.9 Hz, 1H), 3.91 (d, *J* = 6.5 Hz, 2H), 3.50 – 3.32 (m, 2H), 3.16 – 2.94 (m, 1H), 2.55 – 2.38 (m, 1H), 1.75 (s, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 153.2, 141.0, 138.4, 137.3, 136.5, 130.6, 129.7, 129.4, 129.0, 127.4, 127.4, 127.1, 126.8, 126.5, 125.0, 113.1, 113.0, 77.5, 77.2, 76.9, 65.4, 60.3, 56.1, 53.0, 50.6, 46.5, 46.4, 19.3 ppm; IR (KBr): ῡ = 3062, 3029, 2954, 1726, 1642, 1265, 739, 701 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{31}H_{26}O_2N_2Na^{+}$ 481.1886, found 481.1887.

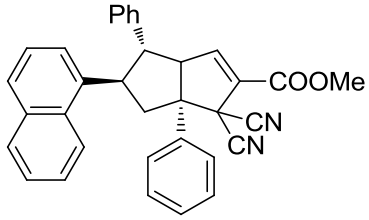
methyl 5-(2-bromophenyl)-1,1-dicyano-4,6a-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2- carboxylate 3r.



White solid; mp: 171-172°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 2H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.46 – 7.40 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.18 (m, 4H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.01 (td, *J* = 7.9, 1.5 Hz, 1H), 4.22 (d, *J* = 5.5 Hz, 1H), 3.92 (s, 3H), 3.86 – 3.76 (m, 1H), 3.51 (dd, *J* = 11.2, 6.1 Hz, 1H), 3.18 (dd, *J* = 12.3, 4.3 Hz, 1H), 2.33 (t, *J* = 12.7 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 152.9, 140.2, 138.1, 133.3, 129.5, 129.3, 129.1, 128.7, 127.9, 127.5, 127.4, 127.2, 127.0, 125.4, 113.1, 112.8, 77.5, 77.2, 76.8, 65.3, 60.5, 54.3, 53.0, 50.4, 48.5, 46.1 ppm; IR

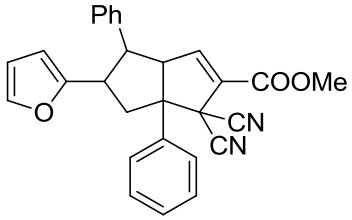
(KBr): ῡ = 3062, 3030, 2954, 1725, 1642, 1263, 751, 700 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{30}H_{23}BrO_2N_2Na^+$ 545.0835, found 545.0837.

methyl 1,1-dicyano-6a-(naphthalen-1-yl)-4,5-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3s.



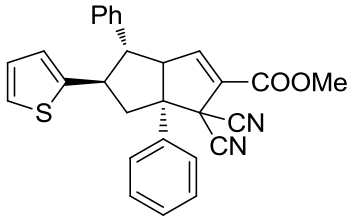
White solid; mp: 117-118°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 3H), 7.71 (dd, *J* = 16.9, 7.8 Hz, 3H), 7.67 – 7.60 (m, 1H), 7.54 (s, 2H), 7.45 (dd, *J* = 14.2, 7.4 Hz, 3H), 7.35 (d, *J* = 6.9 Hz, 1H), 7.30 – 7.18 (m, 5H), 4.41 (s, 1H), 4.24 – 4.04 (m, 1H), 3.98 (s, 3H), 3.84 – 3.72 (m, 1H), 3.40 – 3.27 (m, 1H), 2.55 (dd, *J* = 17.2, 8.3 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 153.1, 140.8, 138.6, 134.9, 133.9, 132.0, 129.8, 129.5, 129.1, 129.0, 127.8, 127.5, 127.4, 127.1, 126.2, 125.6, 125.5, 122.6, 122.3, 113.1, 112.9, 77.5, 77.1, 76.8, 65.4, 60.2, 54.0, 53.0, 50.5, 47.3, 44.9 ppm; IR (KBr): ῡ = 3061, 3032, 2954, 1725, 1642, 1264, 740, 701 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{34}H_{26}O_2N_2Na^+$ 517.1886, found 517.1889.

methyl 1,1-dicyano-5-(furan-2-yl)-4,6a-diphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3t.



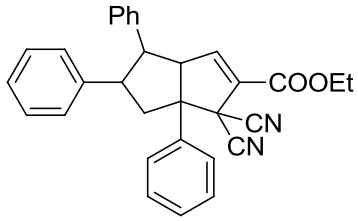
White solid; mp: 195-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.35 (s, 1H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 7.1 Hz, 1H), 7.23 (s, 1H), 7.13 (d, *J* = 7.1 Hz, 2H), 6.25 – 6.13 (m, 1H), 5.86 (d, *J* = 2.6 Hz, 1H), 4.18 (d, *J* = 5.6 Hz, 1H), 3.91 (s, 3H), 3.40 (dd, *J* = 11.0, 5.9 Hz, 1H), 3.29 (tt, *J* = 19.4, 9.6 Hz, 1H), 3.06 (dd, *J* = 12.4, 4.4 Hz, 1H), 2.65 (t, *J* = 12.6 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 153.1, 153.0, 141.7, 140.8, 138.1, 129.6, 129.4, 129.1, 127.5, 127.3, 127.1, 113.1, 112.8, 110.2, 106.2, 77.4, 77.1, 76.8, 65.6, 59.9, 54.1, 53.0, 50.4, 44.5, 43.7 ppm; IR (KBr): ῡ = 3062, 3031, 2954, 1726, 1643, 1252, 739, 701 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{28}H_{25}O_3N_2Na^+$ 457.1523, found 457.1529.

methyl 1,1-dicyano-4,6a-diphenyl-5-(thiophen-2-yl)-1,3a,4,5,6,6a-hexahydropentalene- 2-carboxylate 3u.



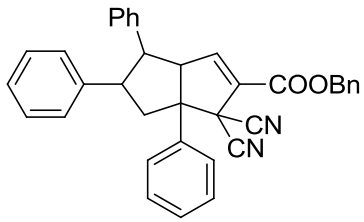
White solid; mp: 187-188°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 22.7 Hz, 2H), 7.63 (t, *J* = 6.9 Hz, 2H), 7.58 (d, *J* = 6.6 Hz, 1H), 7.46 – 7.32 (m, 4H), 7.23 (d, *J* = 6.7 Hz, 2H), 7.10 (t, *J* = 8.7 Hz, 1H), 6.92 – 6.83 (m, 1H), 6.68 (d, *J* = 13.3 Hz, 1H), 4.28 (d, *J* = 4.1 Hz, 1H), 3.98 (s, 3H), 3.58 (dd, *J* = 15.3, 8.0 Hz, 1H), 3.35 – 3.23 (m, 2H), 2.73 (t, *J* = 12.6 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 152.9, 143.2, 140.6, 138.3, 129.8, 129.5, 129.2, 127.7, 127.4, 127.1, 126.8, 124.4, 123.8, 113.1, 112.8, 77.6, 77.3, 76.9, 65.4, 60.3, 57.8, 53.0, 50.6, 47.1, 45.5 ppm; IR (KBr): ῡ = 3063, 3031, 2954, 1726, 1643, 1252, 739, 701 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{28}H_{22}O_2N_2SNa^+$ 473.1294, found 473.1301.

ethyl 1,1-dicyano-4,5,6a-triphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3v.



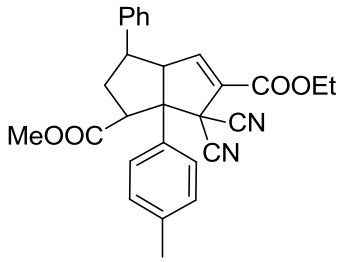
White solid; mp: 120-121 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.52 (dt, *J* = 19.9, 6.8 Hz, 3H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 7.4 Hz, 2H), 7.16 (d, *J* = 6.9 Hz, 3H), 7.09 (d, *J* = 7.0 Hz, 2H), 7.00 (d, *J* = 6.4 Hz, 2H), 4.44 – 4.30 (m, 2H), 4.22 (s, 1H), 3.39 – 3.16 (m, 2H), 3.15 – 3.00 (m, 1H), 2.66 (t, *J* = 12.4 Hz, 1H), 1.47 – 1.33 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 152.9, 141.1, 139.4, 138.6, 129.7, 129.3, 129.1, 128.6, 127.7, 127.6, 127.4, 127.2, 127.1, 113.3, 113.0, 77.6, 77.3, 76.9, 65.4, 62.4, 60.4, 57.0, 50.7, 50.2, 46.2, 14.1 ppm; IR (KBr): ῡ = 3062, 3030, 2957, 1721, 1642, 1249, 745, 699 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{31}H_{26}O_2N_2Na^+$ 481.1886, found 481.1889.

benzyl 1,1-dicyano-4,5,6a-triphenyl-1,3a,4,5,6,6a-hexahydropentalene-2-carboxylate 3w.



White solid; mp: 204-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.54 (dd, *J* = 14.8, 7.6 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.44 (t, *J* = 8.3 Hz, 2H), 7.42 – 7.32 (m, 4H), 7.29 – 7.20 (m, 3H), 7.19 – 7.12 (m, 3H), 7.12 – 7.01 (m, 2H), 6.99 (d, *J* = 6.4 Hz, 2H), 5.34 (s, 2H), 4.21 (s, 1H), 3.22 (d, *J* = 3.0 Hz, 2H), 3.04 (t, *J* = 17.3 Hz, 1H), 2.67 (dd, *J* = 9.4, 2.8 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 153.3, 141.0, 139.3, 138.5, 134.7, 129.7, 129.4, 129.1, 128.8, 128.7, 128.6, 127.6, 127.4, 127.4, 127.2, 127.1, 113.2, 112.9, 77.5, 77.2, 76.8, 68.1, 65.4, 60.4, 56.9, 50.6, 50.2, 46.2 ppm; IR (KBr): ῡ = 3061, 3031, 2955, 1727, 1643, 1265, 743, 700 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{36}H_{28}O_2N_2Na^+$ 543.2043, found 543.2040.

5-ethyl 1-methyl 6,6-dicyano-3-phenyl-6a-(p-tolyl)-1,2,3,3a,6,6a-hexahydropentalene-1,5-dicarboxylate 7.



White solid; mp: 197-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 6H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.38 (dd, *J* = 7.1, 4.3 Hz, 2H), 4.05 (dd, *J* = 7.3, 2.3 Hz, 1H), 3.64 – 3.60 (m, 1H), 3.59 (s, 2H), 3.36 (dt, *J* = 11.2, 7.8 Hz, 1H), 2.66 (d, *J* = 7.3 Hz, 1H), 2.44 (dt, *J* = 24.8, 12.4 Hz, 1H), 2.33 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 160.5, 152.4, 140.8, 138.8, 133.9, 129.1, 129.1, 128.4, 128.2, 127.5, 126.9, 113.1, 113.0, 77.6, 77.3, 76.9, 71.1, 62.7, 62.4, 52.0, 49.6, 47.2, 36.2, 21.1, 14.0 ppm; IR (KBr): ῡ = 3061, 3030, 2954, 1729, 1646, 1262, 741, 701 cm^{-}; HRMS-ESI ([M + Na]+) calcd for $C_{28}H_{26}O_4N_2Na^+$ 477.1785, found 477.1794.

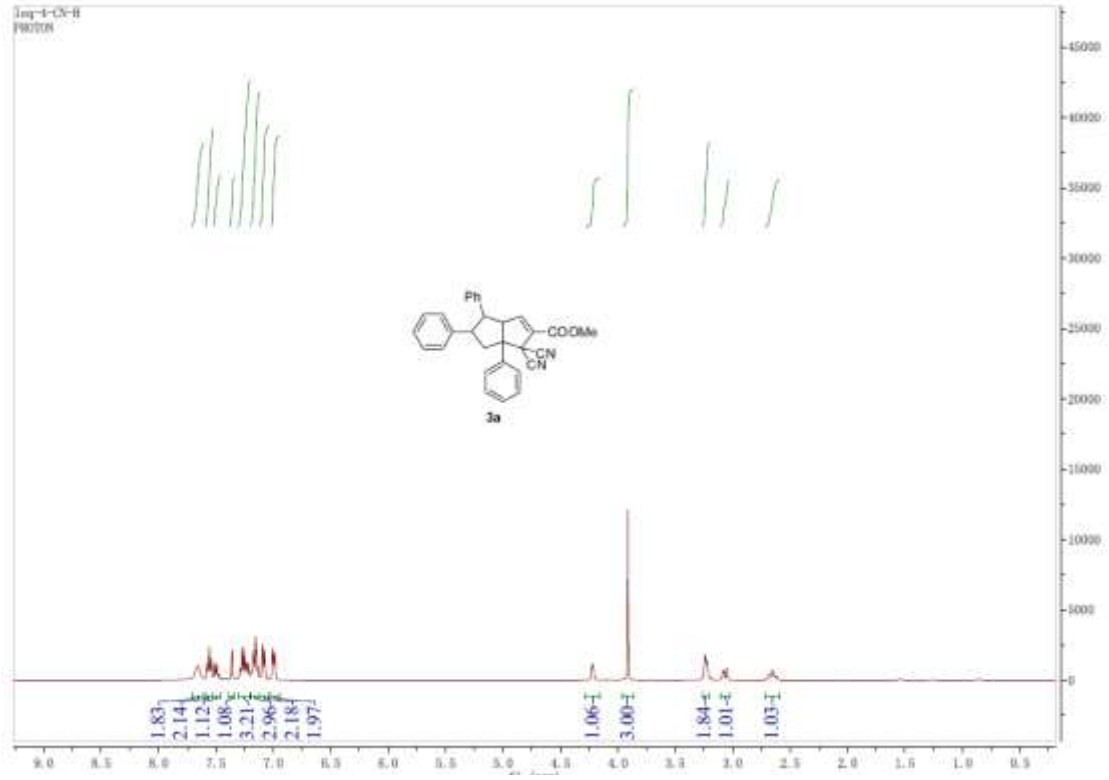
[1]. H. Nakamura, H. Iwama, M. Ito, Y. Yamamoto, *J. Am. Chem. Soc*. 1999**, 121**, 10850.

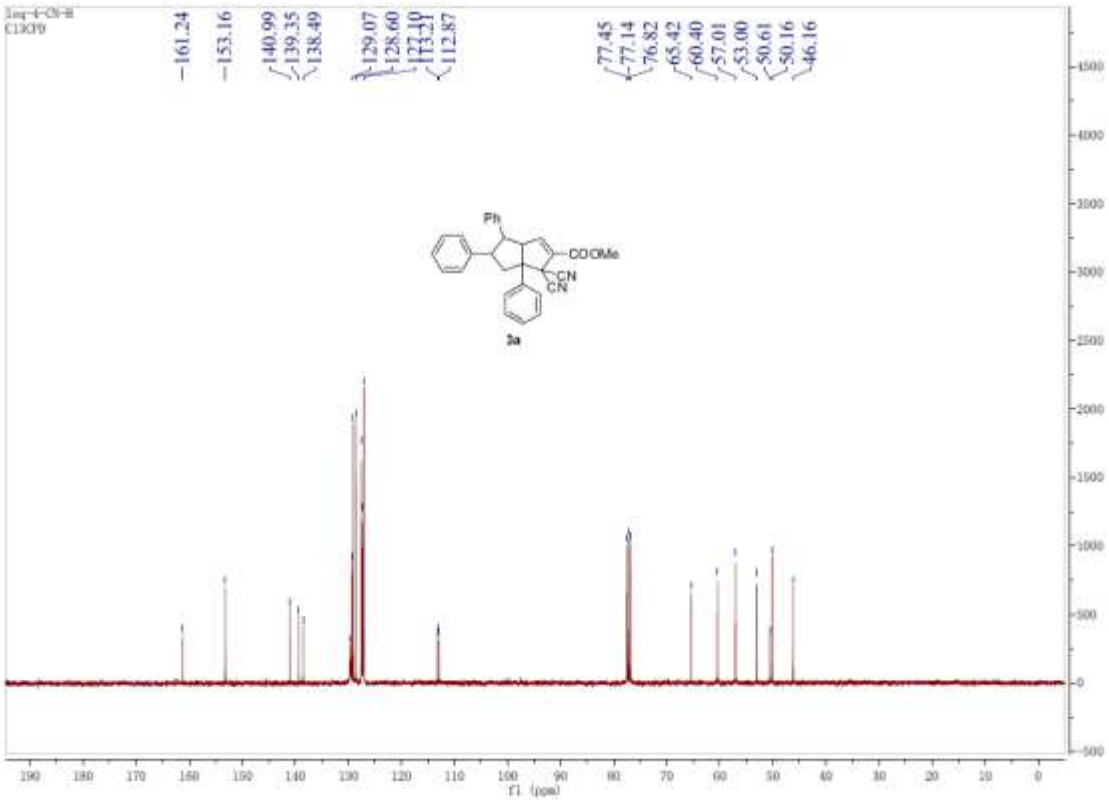
[2]. T.-R. Kang, L.-M. Chen, *Acta Cryst.* 2009. **65**, o3164.

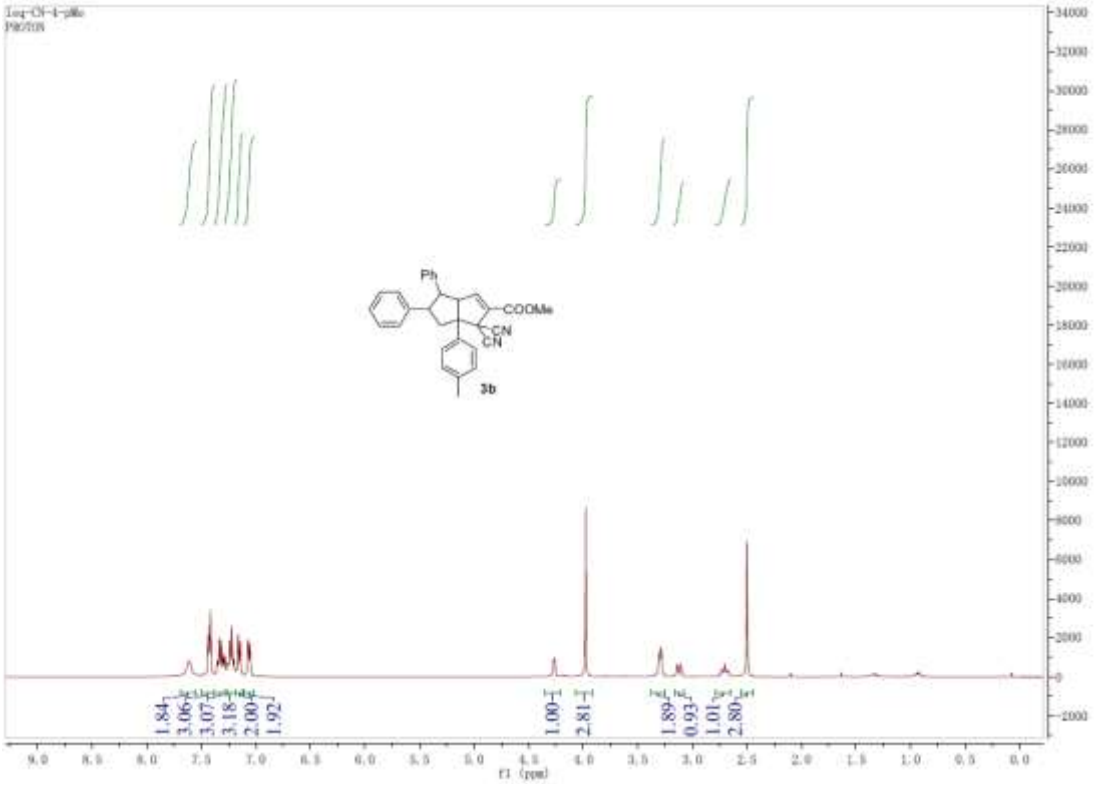
[3]. R. W. Lang, H.-J. Hansen, *Organic Syntheses.* 1990, **62**, 202.

[4]. A. Suarez, G. C. Fu, *Angew.Chem. In. Ed.* 2004, **43,** 3580.

VII. ^{1}H and ^{13}C NMR Spectra



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3.07
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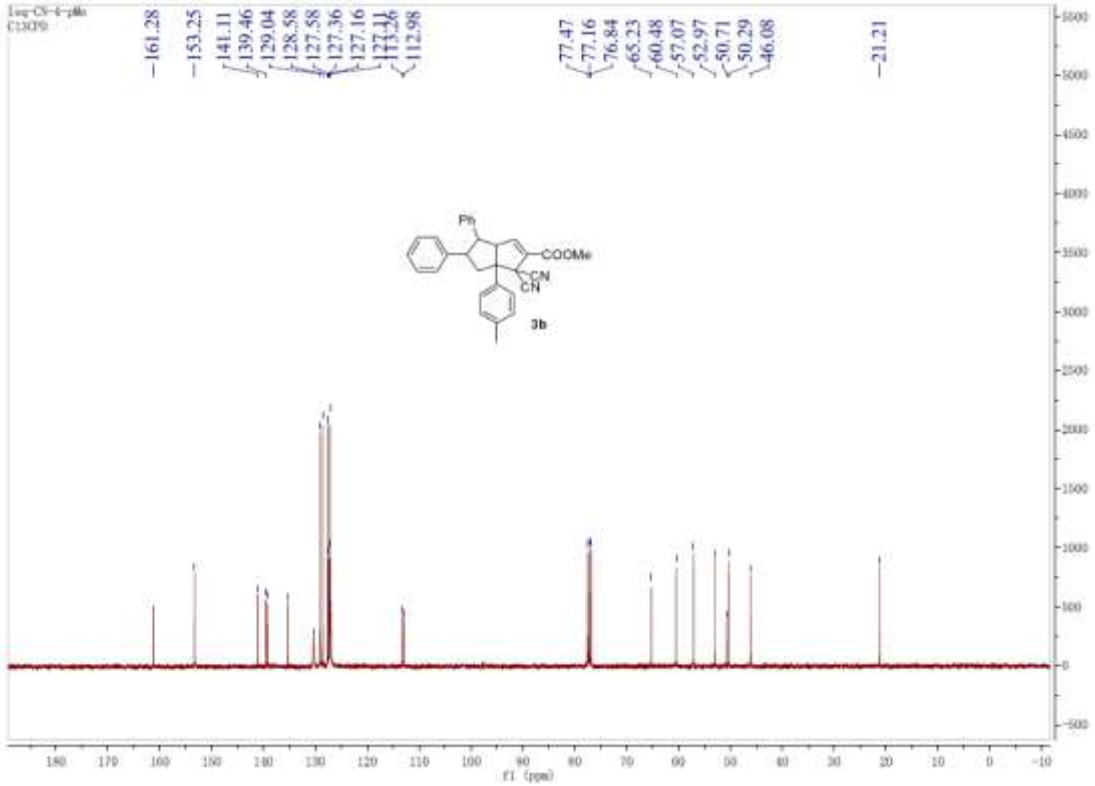
1.00
2.81
1.89
0.93
1.01
2.80
f1 (ppm)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153.25
141.11
139.46
129.04
128.58
127.58
127.36
127.16
127.11
113.26
112.98
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77.16
76.84
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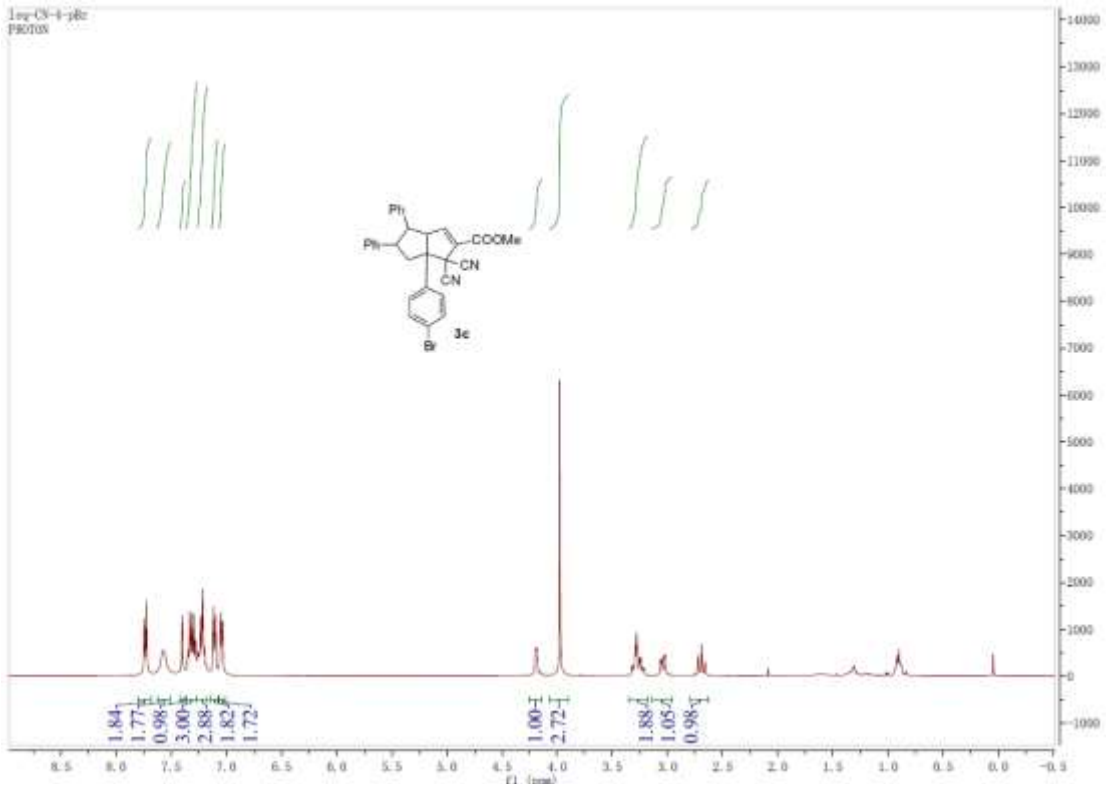
21.21
Ph
COOMe
CN
CN
3b
f1 (ppm)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Ph
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CN
CN
Br
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1.77
0.98
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1.00
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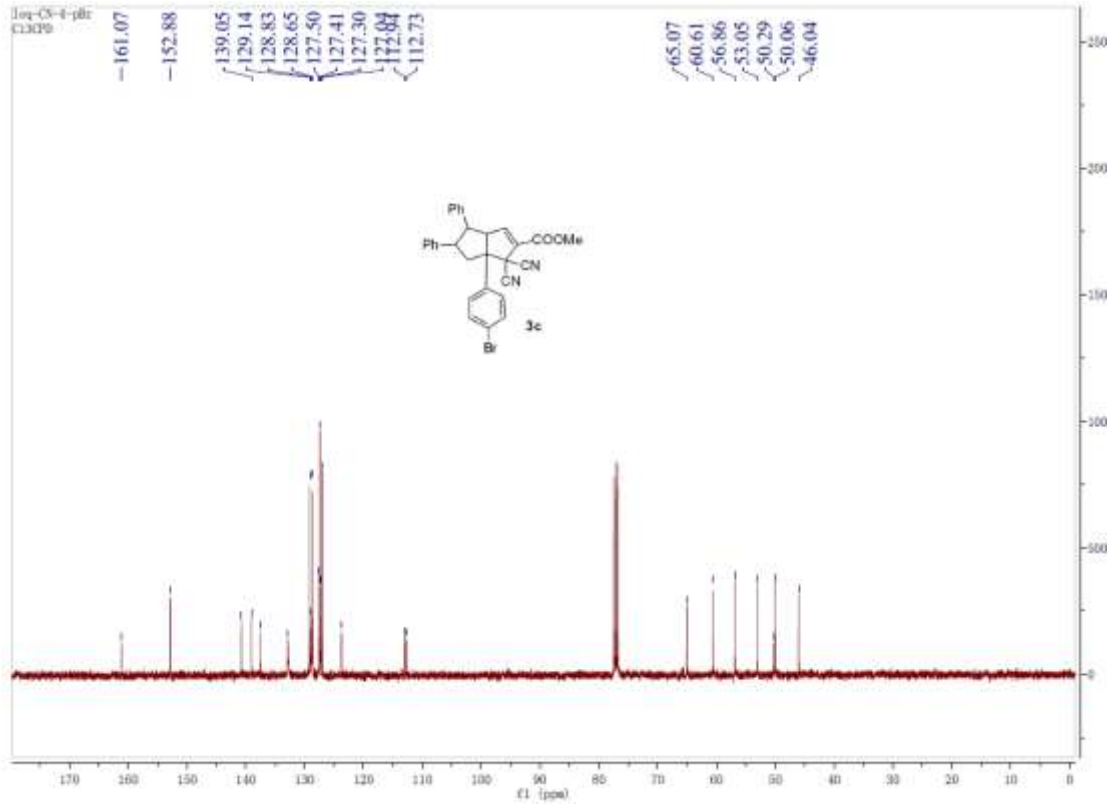
1.88
1.05
0.98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128.83
128.65
127.50
127.41
127.30
112.73
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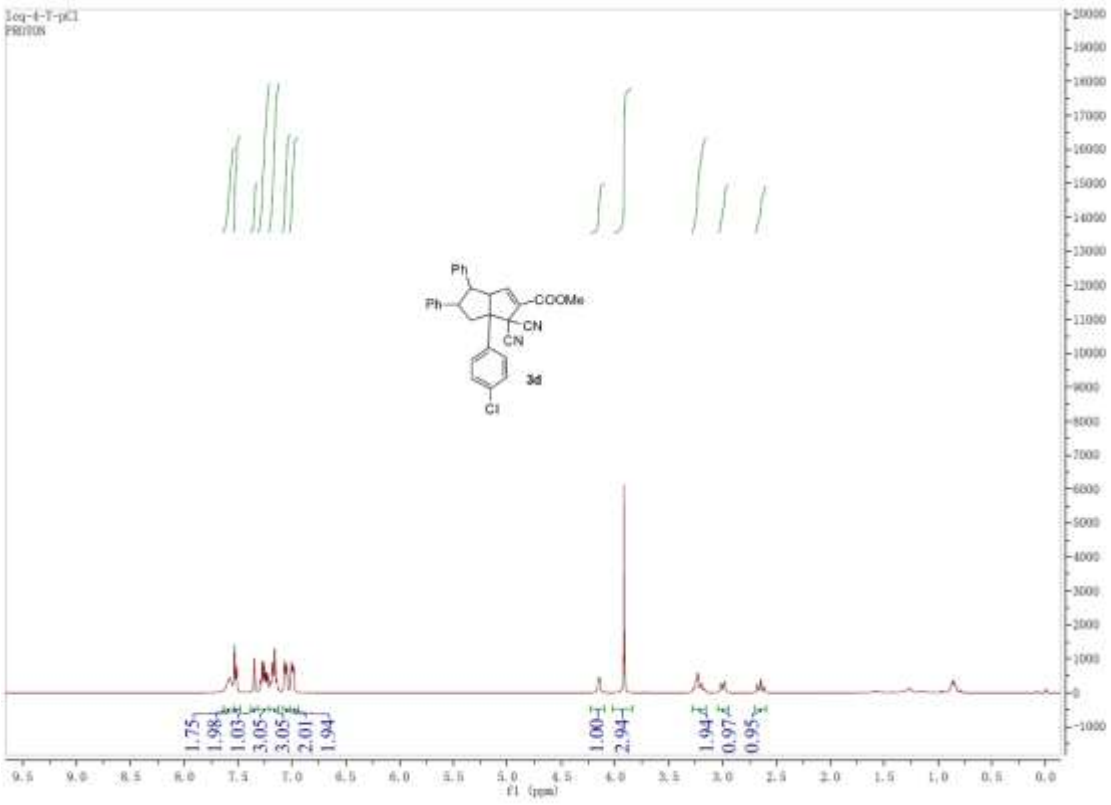
56.86
53.05
50.29
50.06
46.04
Ph
Ph
COOMe
CN
CN
Br
3c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Ph
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CN
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Cl
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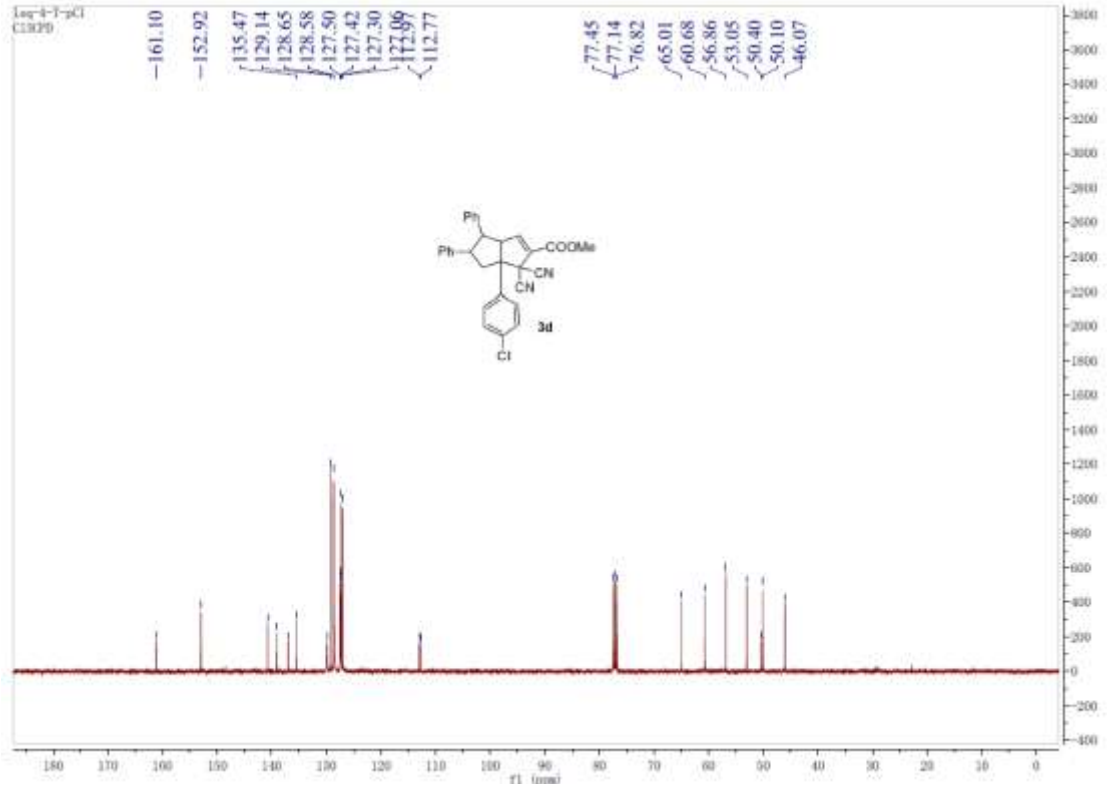
3.05
3.05
2.01
1.94
1.00
2.94
1.94
0.97
0.95
f1 (ppm)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128.58
127.50
127.42
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122.09
112.97
112.77
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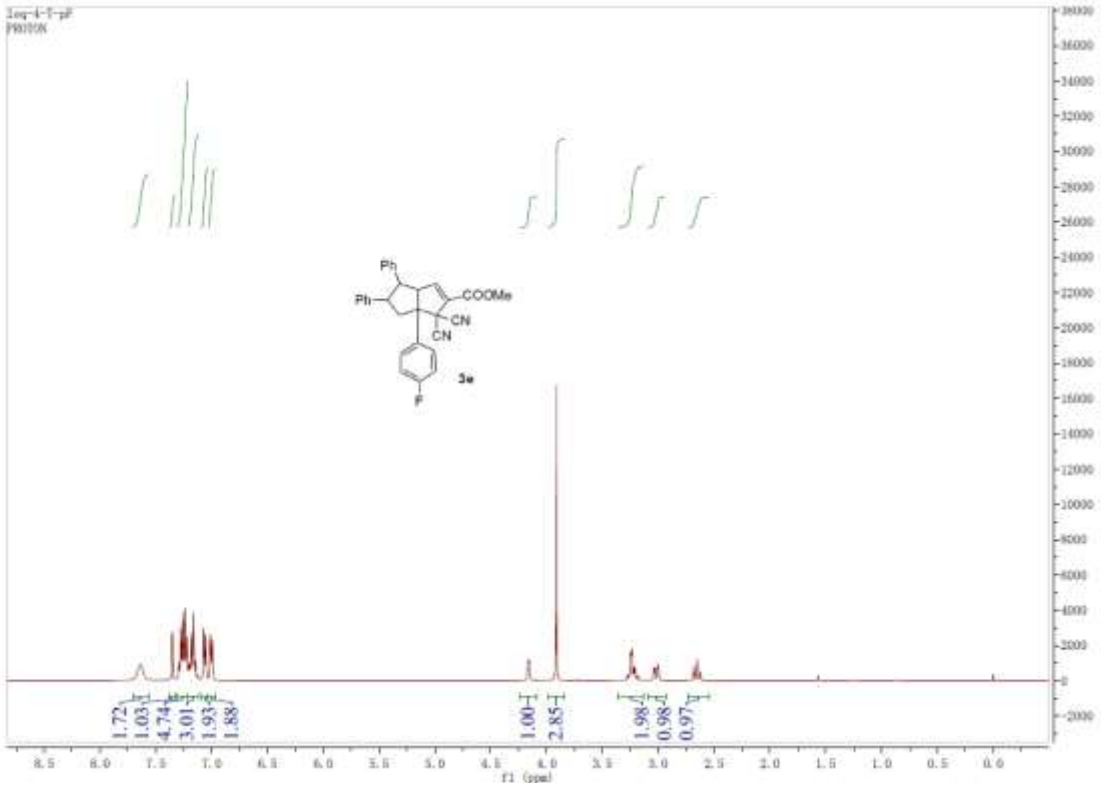
77.14
76.82
65.01
60.68
56.86
53.05
50.40
50.10
46.07
Ph
Ph
COOMe
CN
CN
3d
Cl
f1 (ppm)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Ph
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CN
3e
F
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4.74
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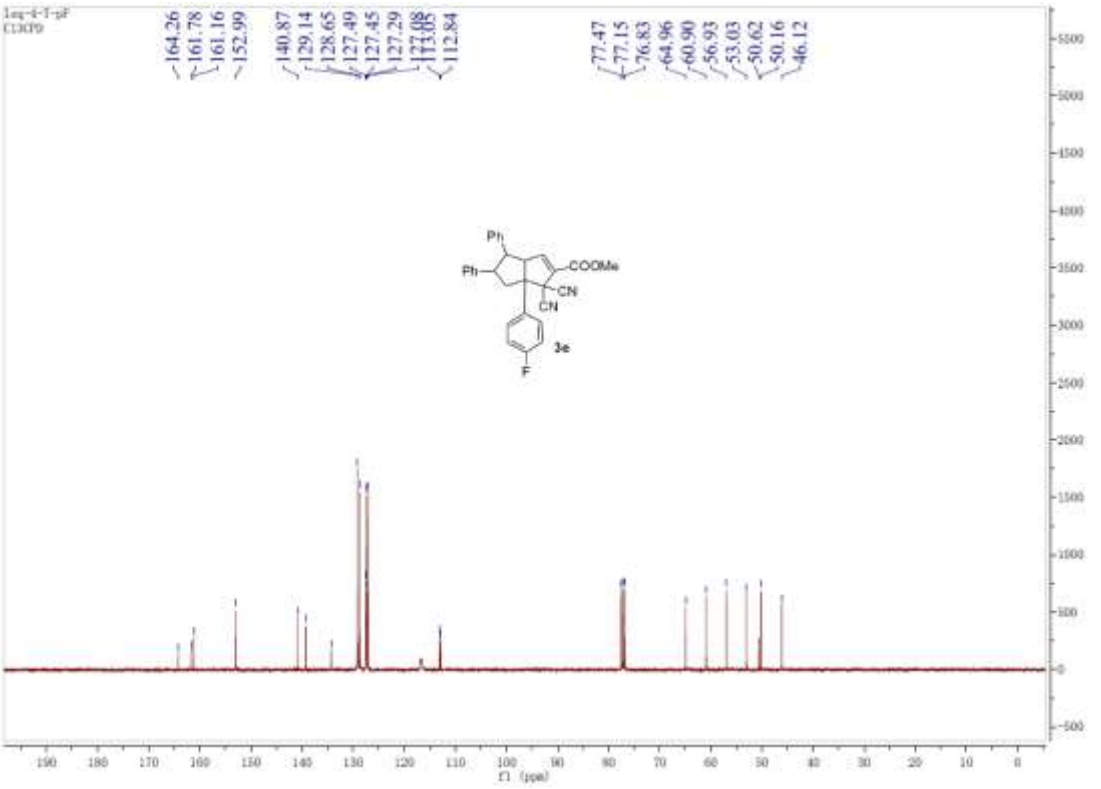
1.88
1.00
2.85
1.98
0.98
0.97
f1 (ppm)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128.65
127.49
127.45
127.29
112.84
77.47
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76.83
64.96
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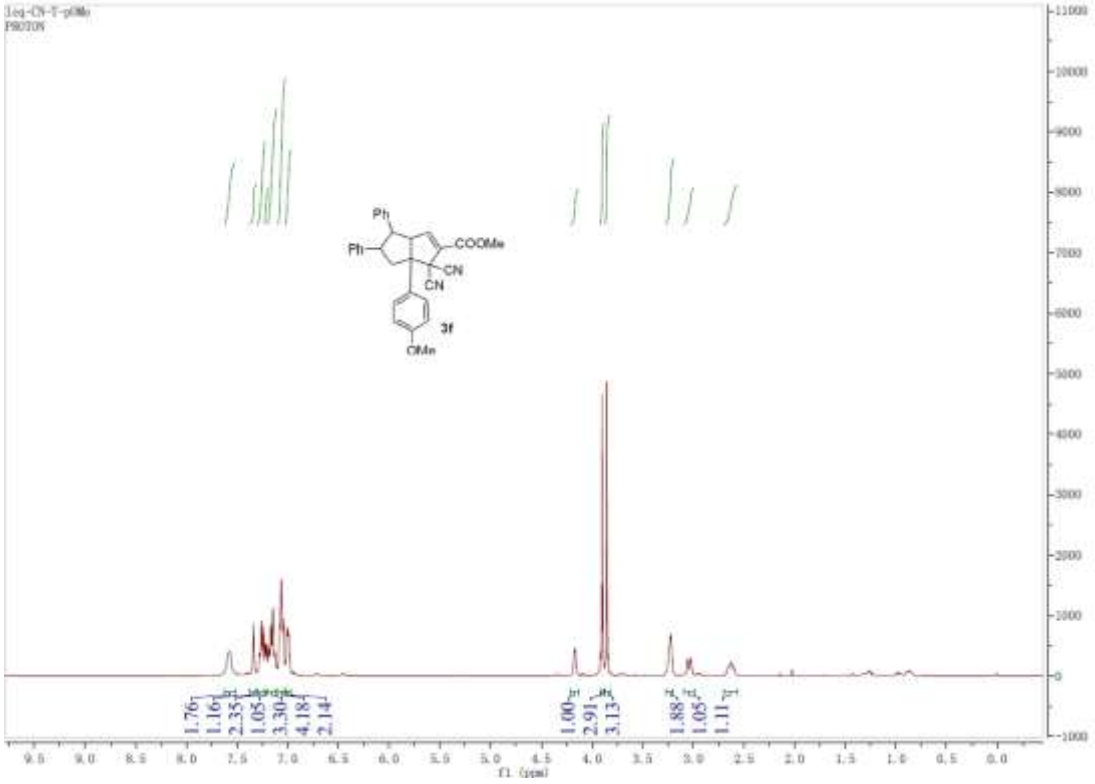
53.03
50.62
50.16
46.12
Ph
Ph
COOMe
CN
CN
3e
F
f1 (ppm)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Ph
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CN
CN
3f
OMe
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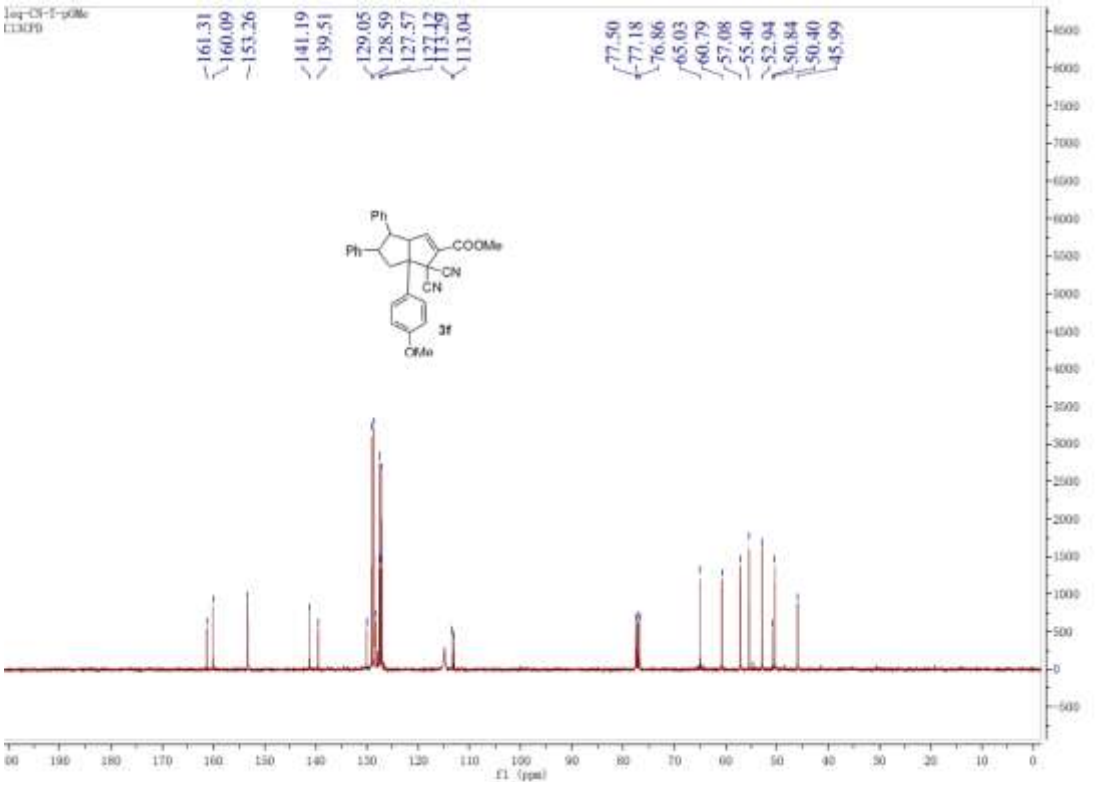
3.30
4.18
2.14
1.00
2.91
3.13
1.88
1.05
1.11
f1 (ppm)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139.51
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128.59
127.57
127.12
113.29
113.04
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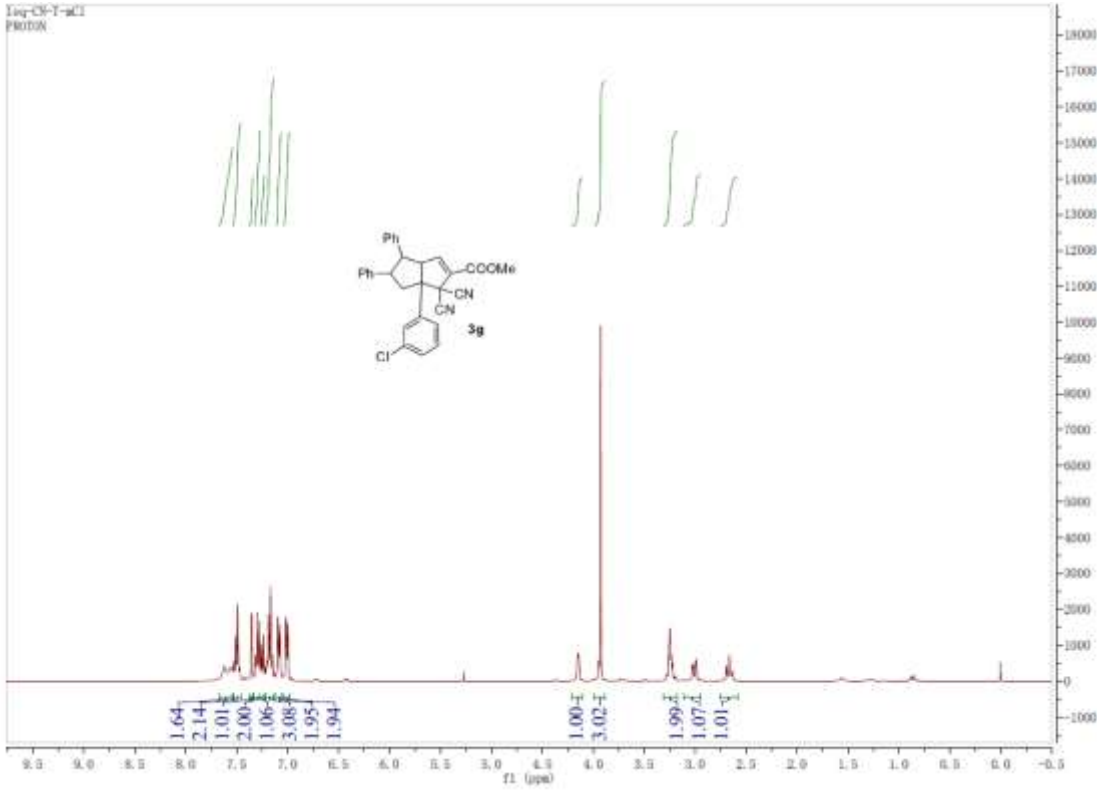
77.18
76.86
65.03
60.79
57.08
55.40
52.94
50.84
50.40
45.99
Ph
Ph
COOMe
CN
CN
3f
OMe
f1 (ppm)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Ph
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CN
Cl
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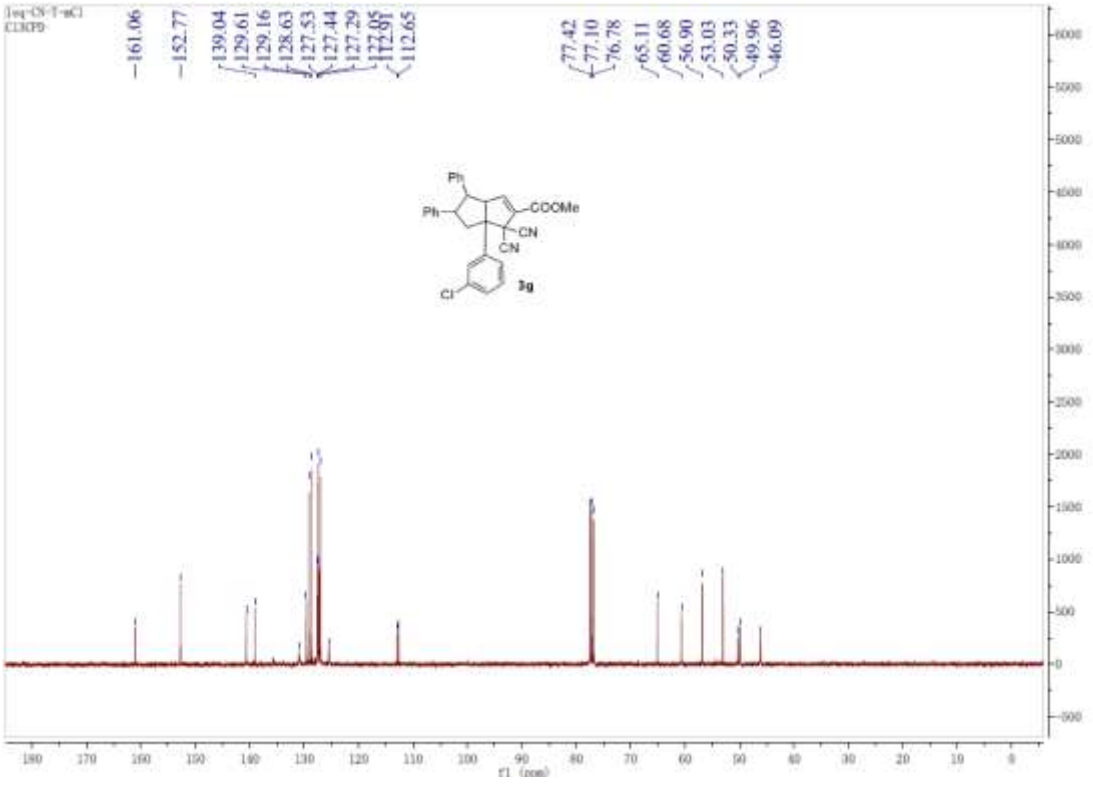
1.99
1.07
1.01
f1 (ppm)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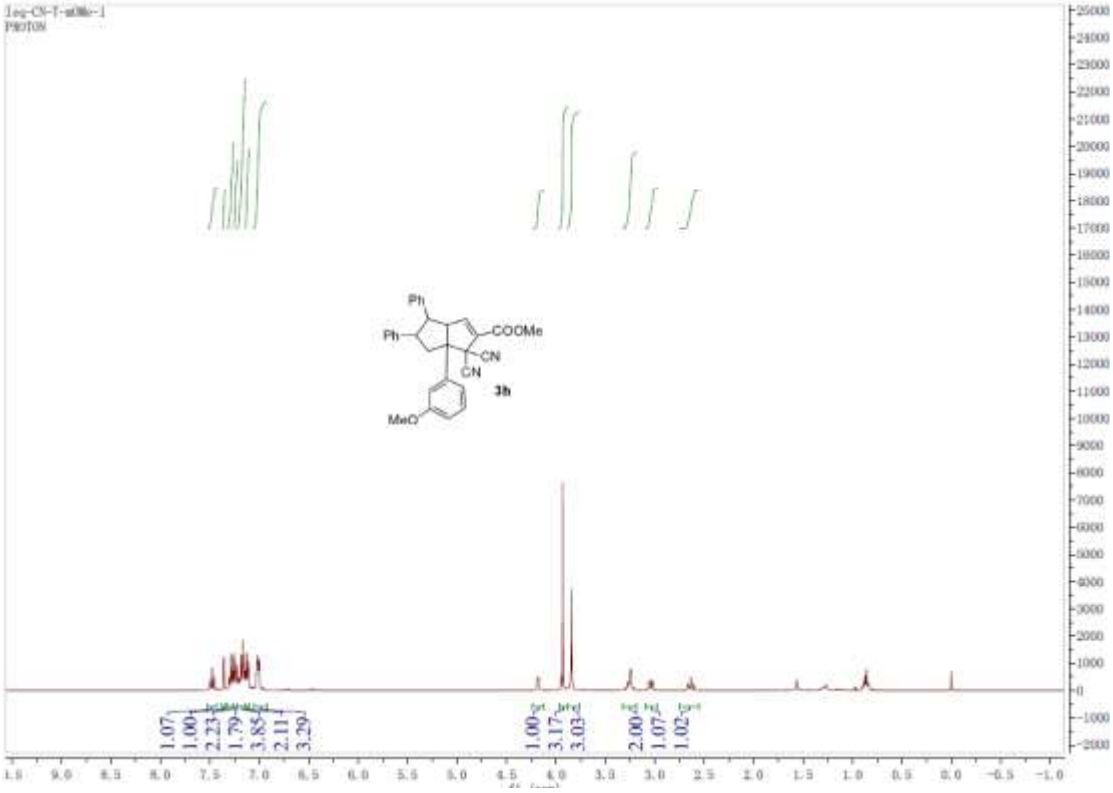
Ph
COOMe
CN
CN
Cl
3g
f1 (ppm)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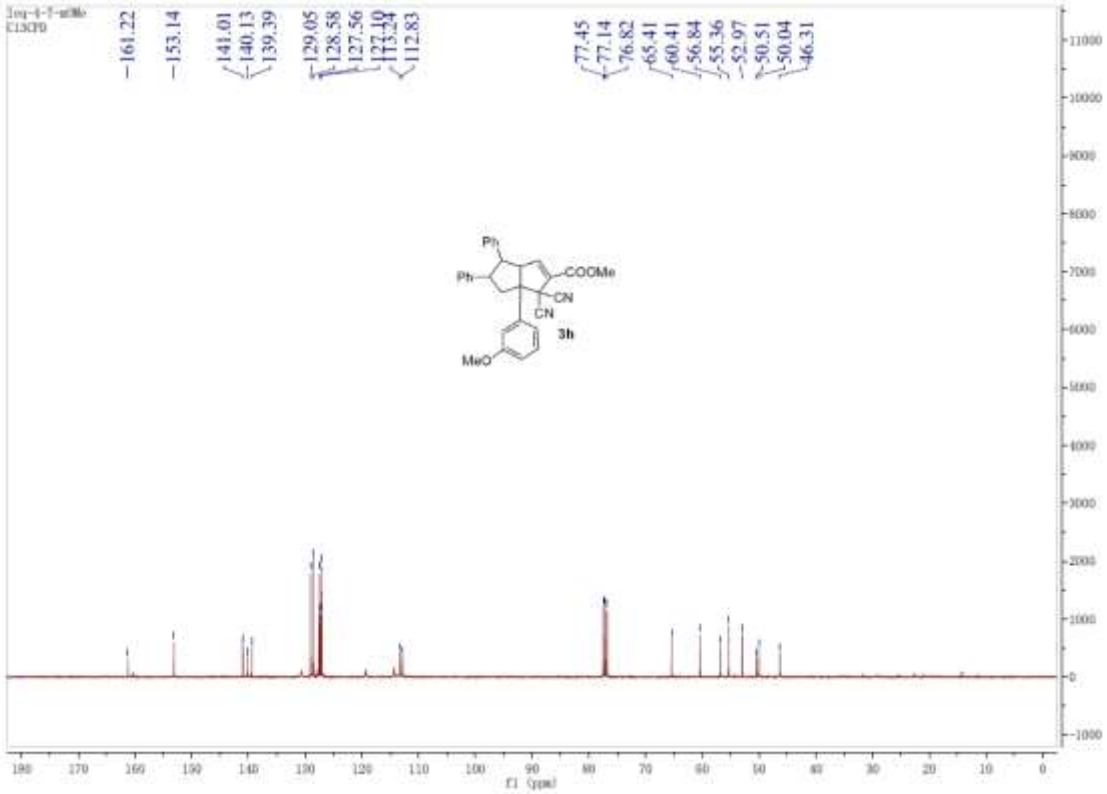
2.00
1.07
1.02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77.14
76.82
65.41
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52.97
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50.04
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Ph
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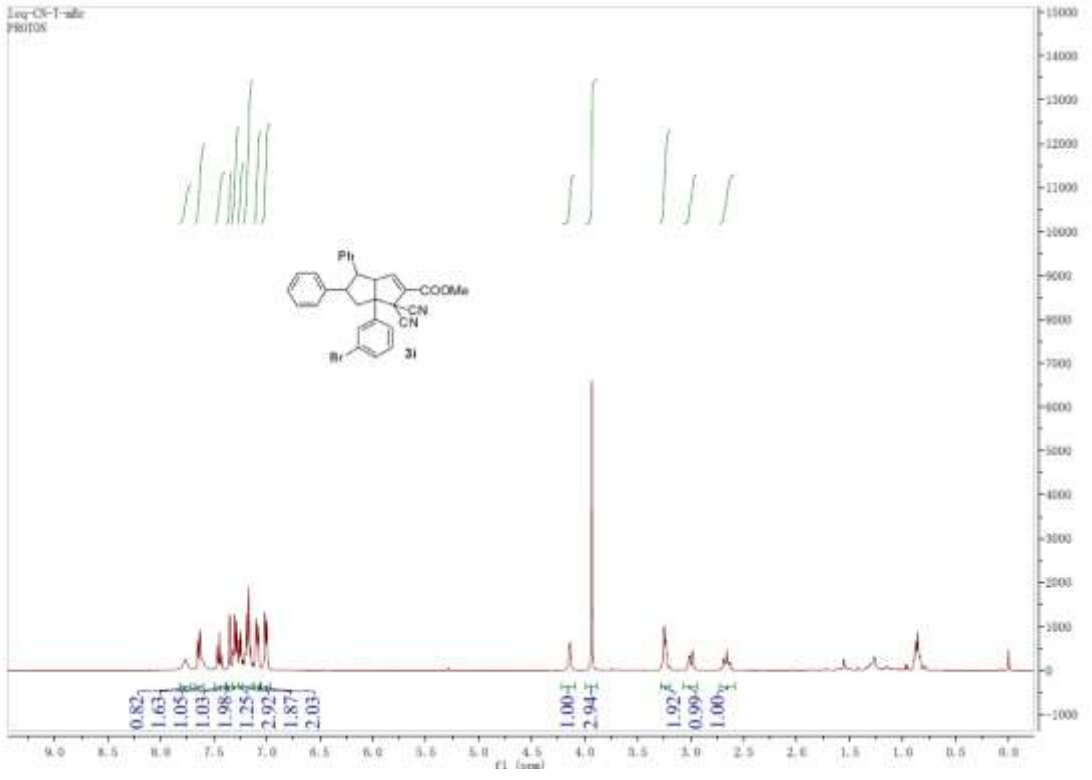
CN
CN
3h
MeO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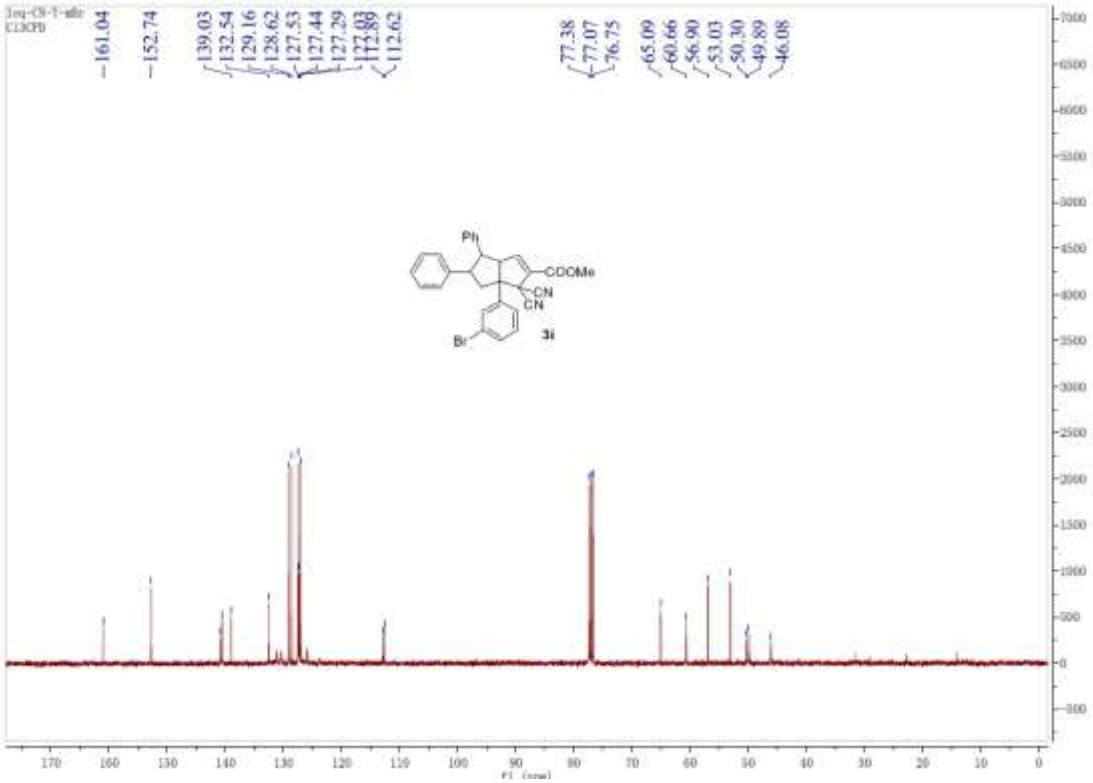
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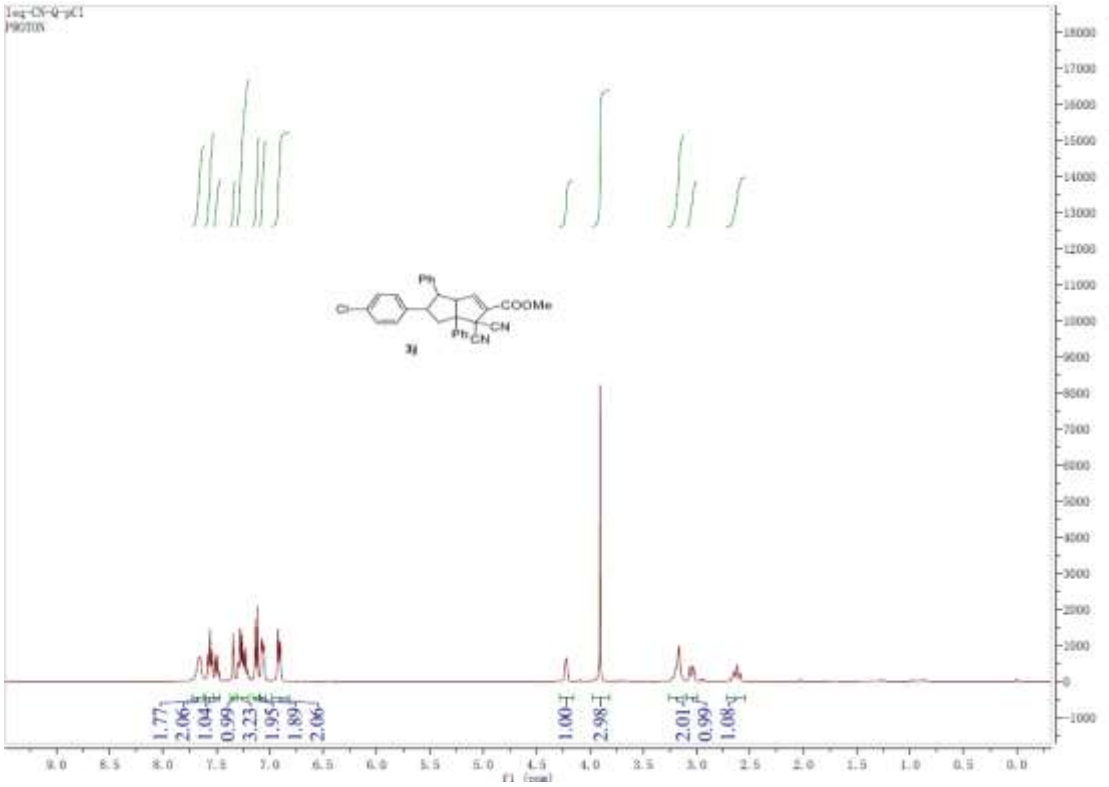
CN
Br
3i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1.08
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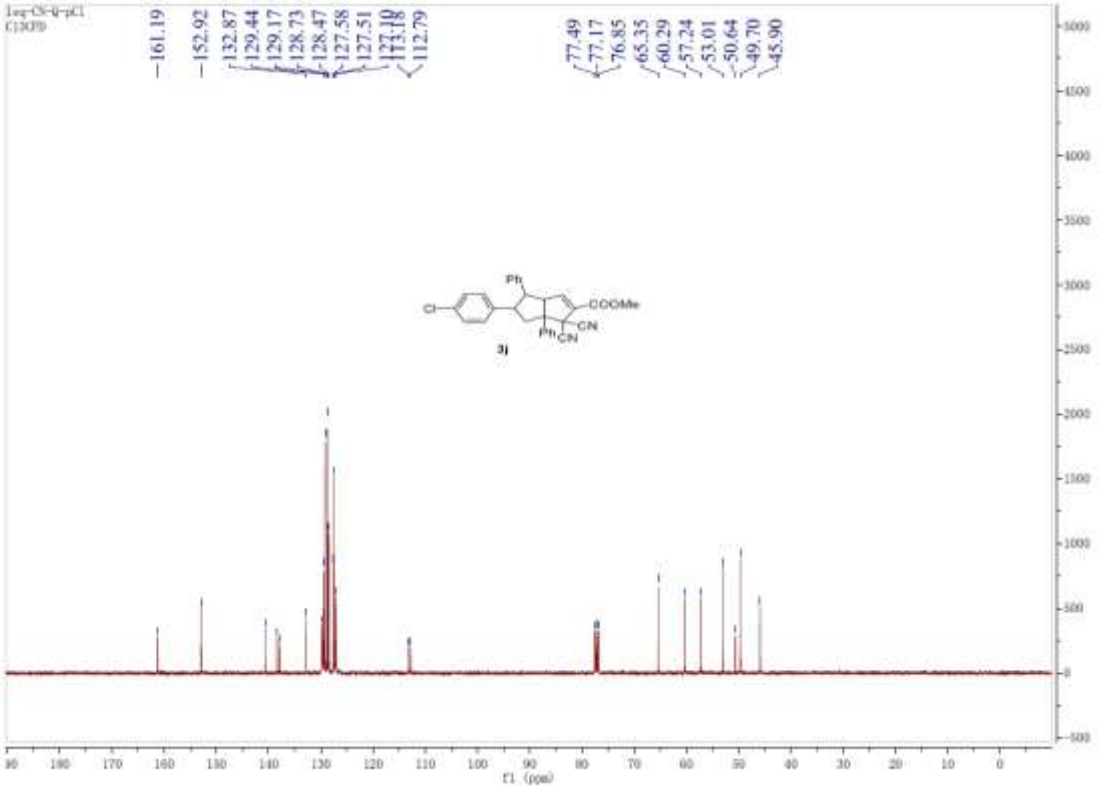
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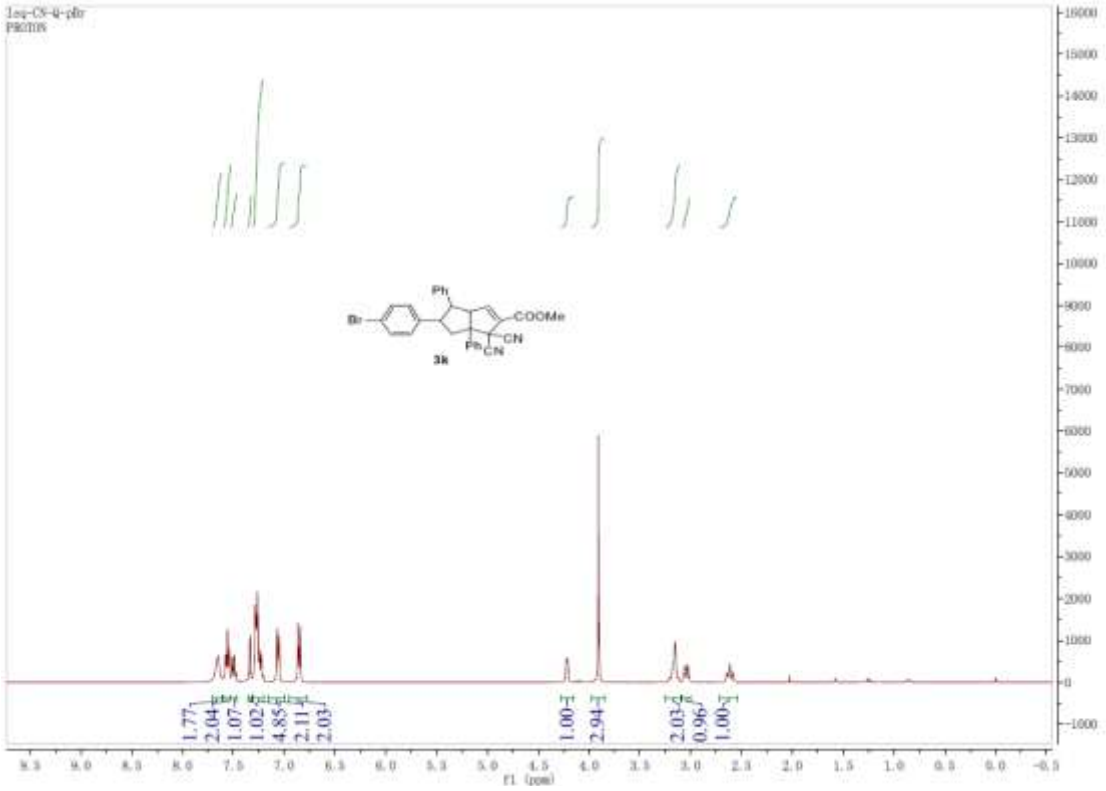
3j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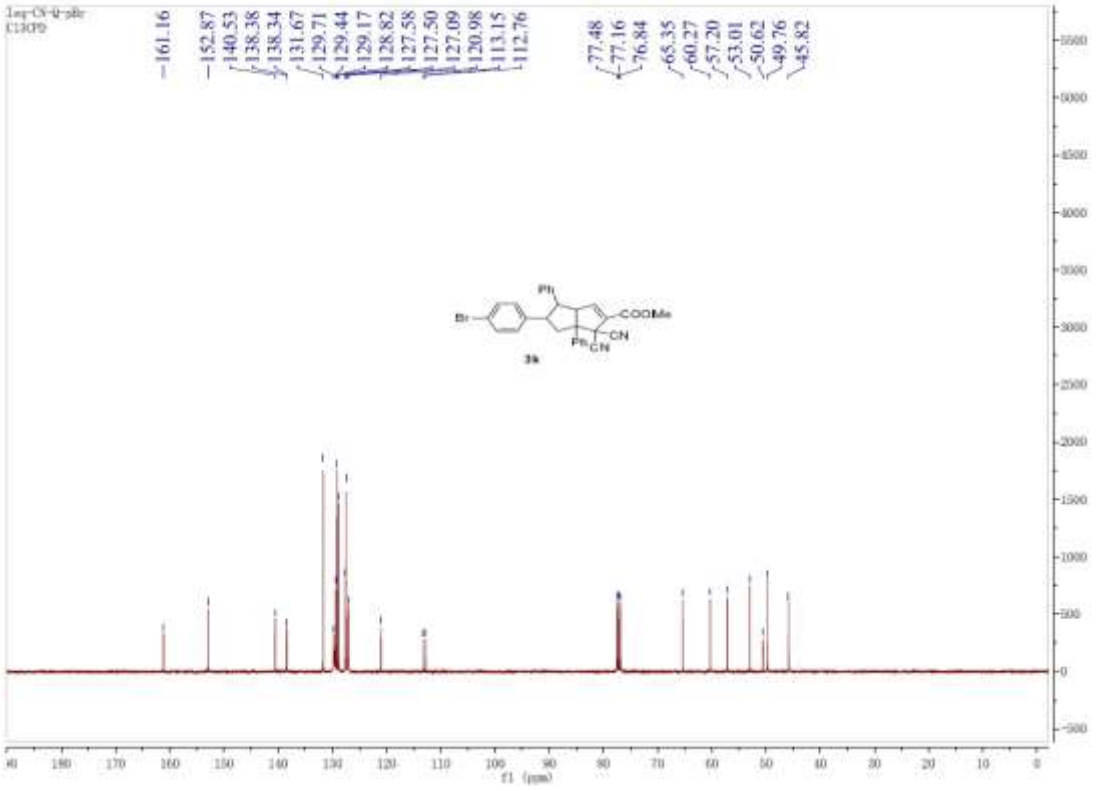
f1 (ppm)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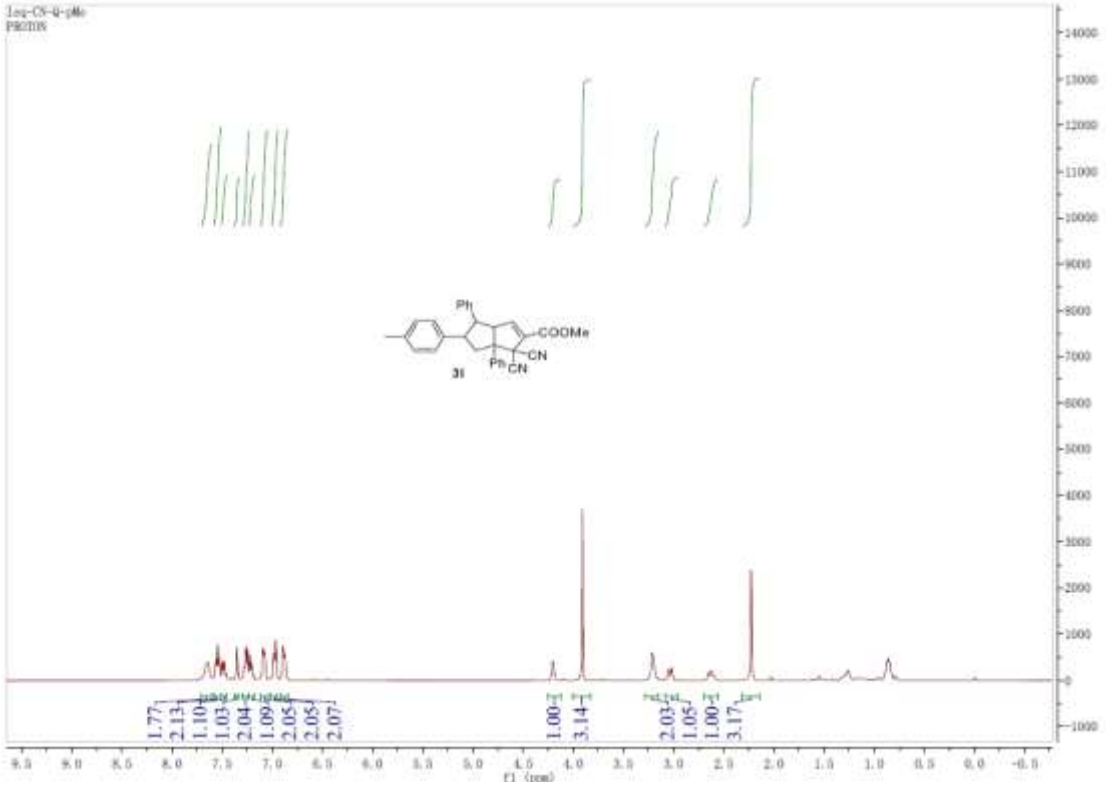
45.82
f1 (ppm)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COOMe
CN
Ph
CN
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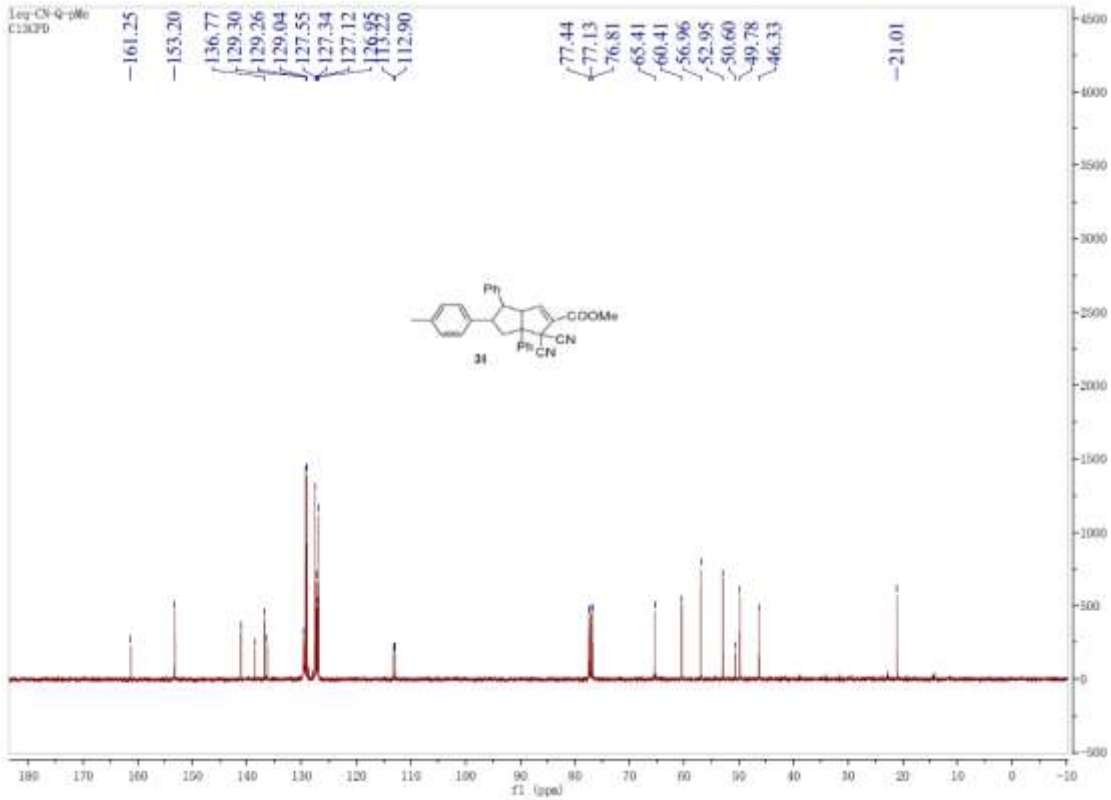
3.17
f1 (ppm)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COOMe
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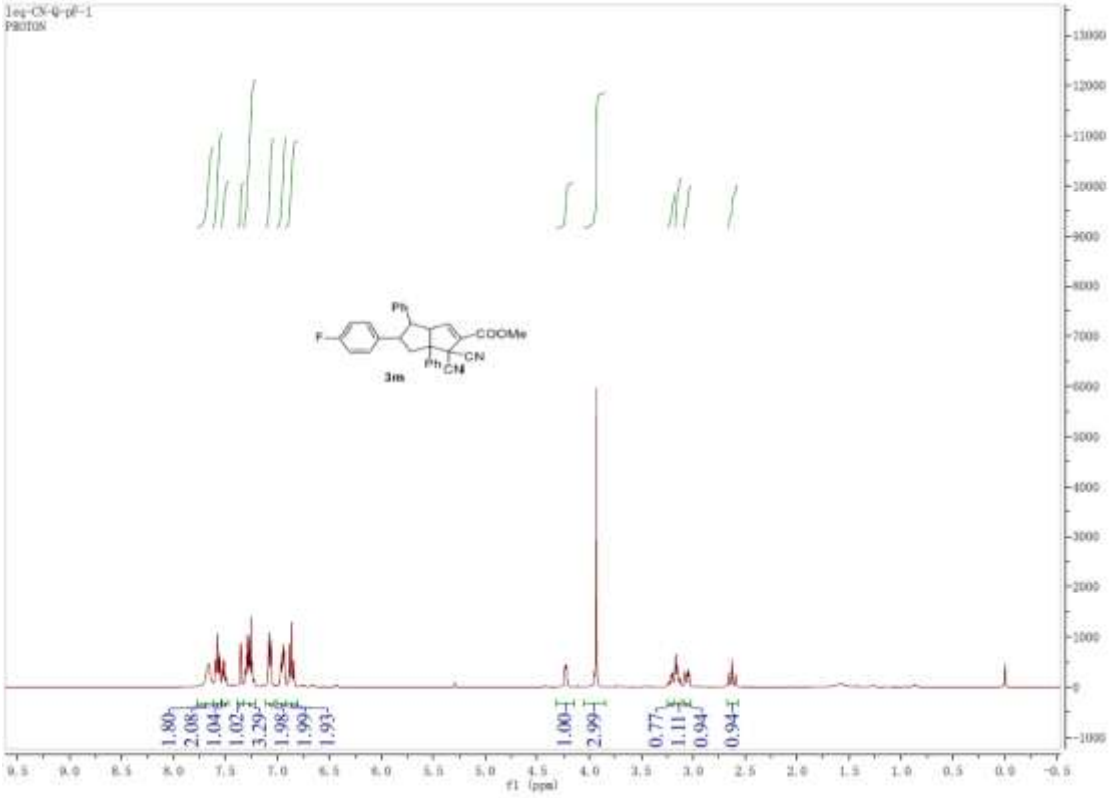
Ph
CN
3l
f1 (ppm)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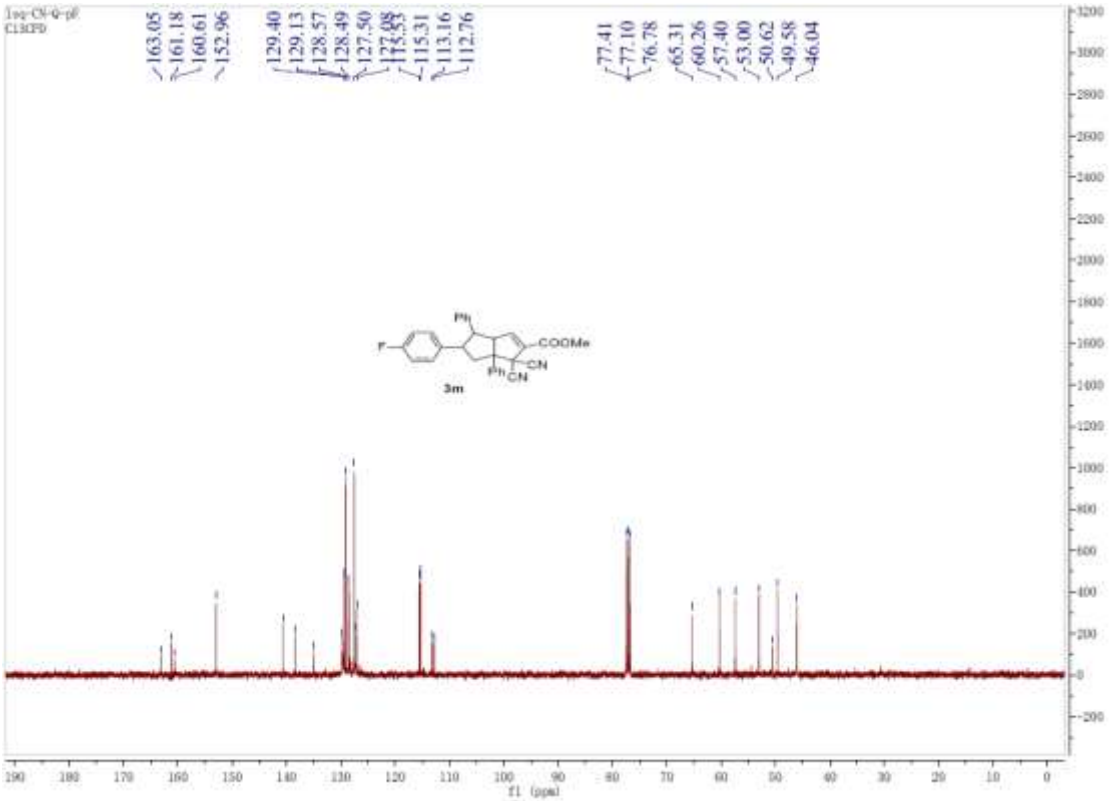
0.94
f1 (ppm)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115.31
113.16
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77.10
76.78
65.31
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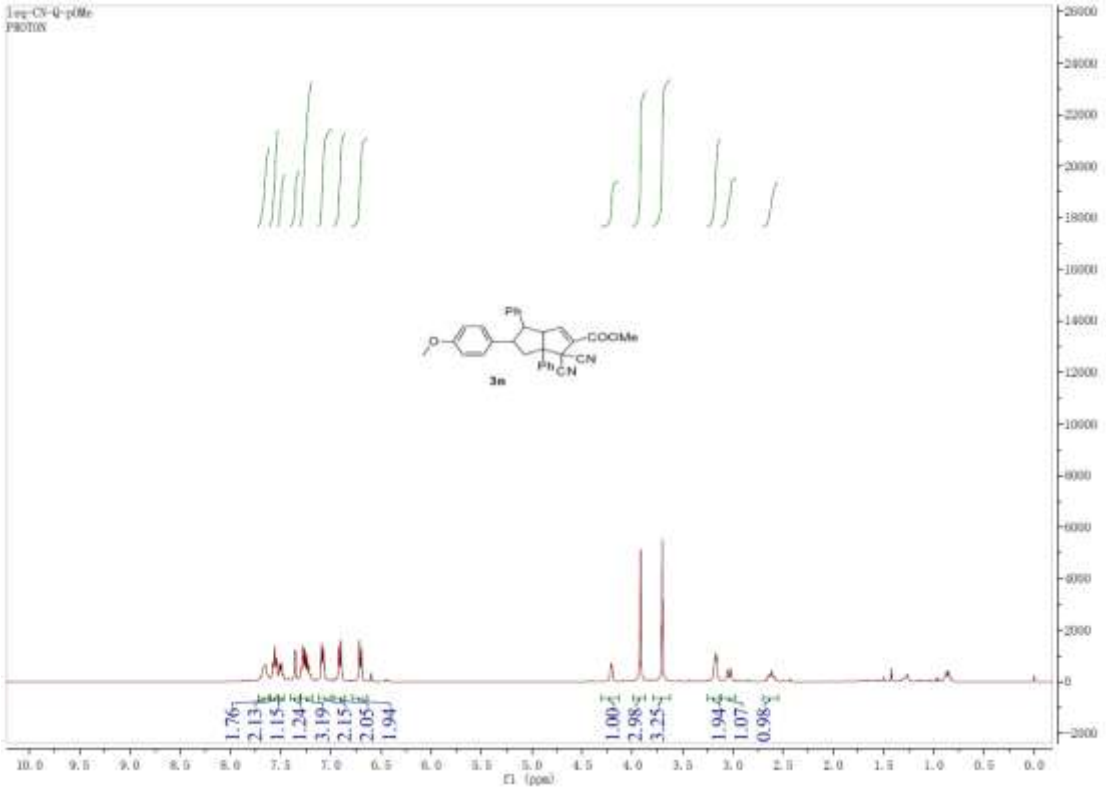
F
COOMe
CN
Ph
CN
3m
f1 (ppm)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2.98
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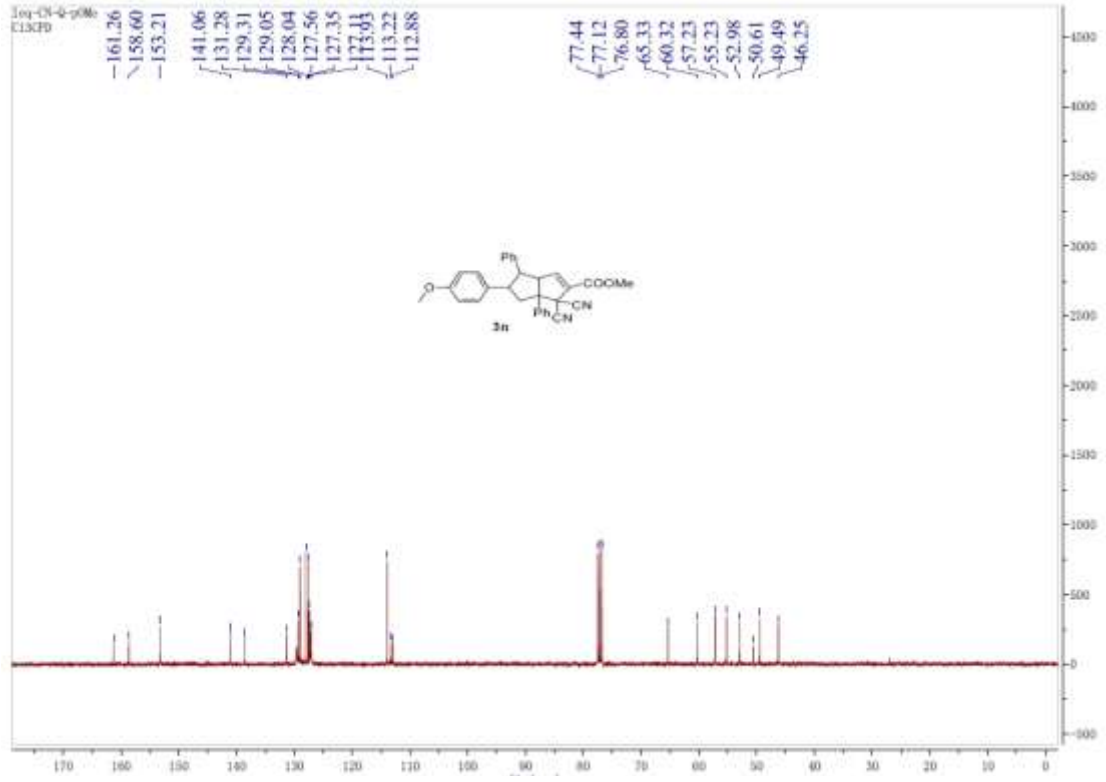
0.98
f1 (ppm)
3n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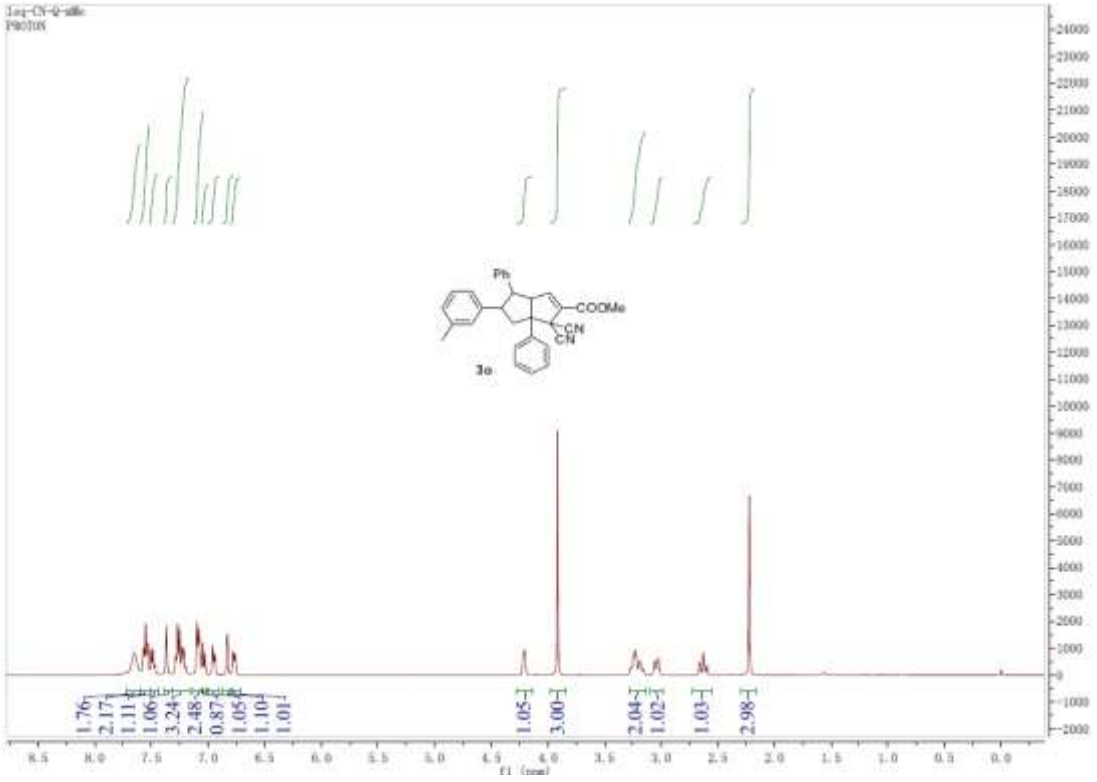
3n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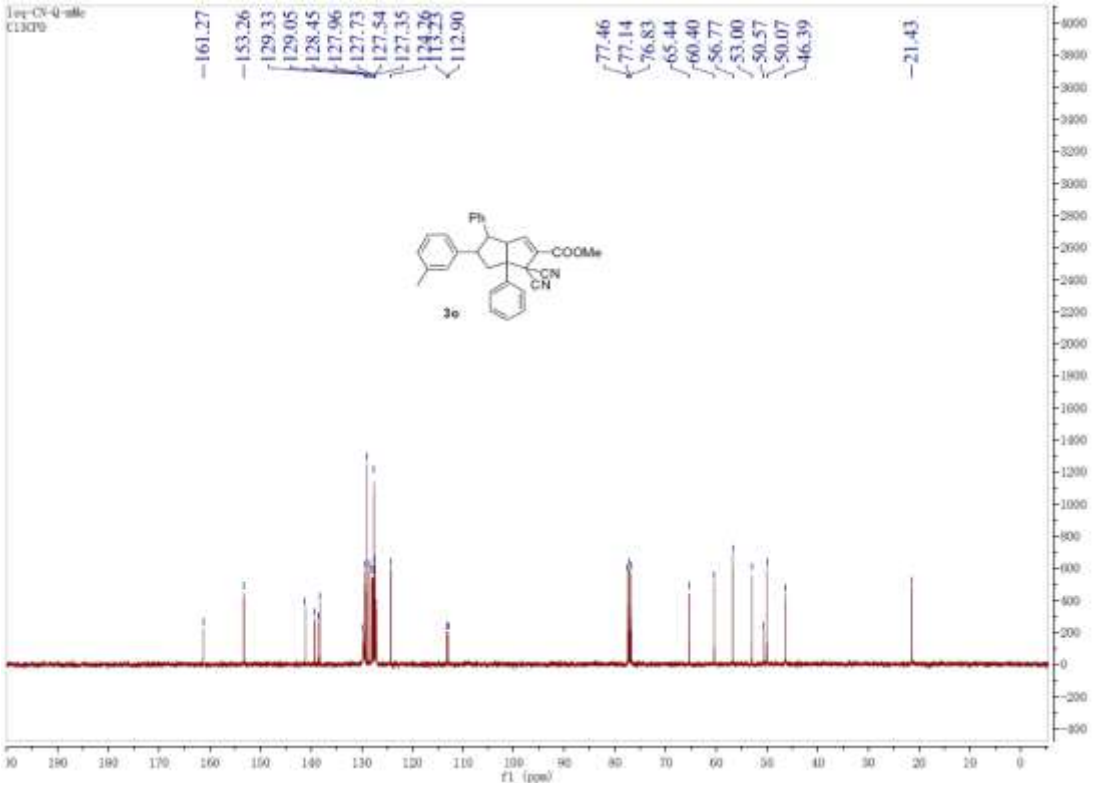
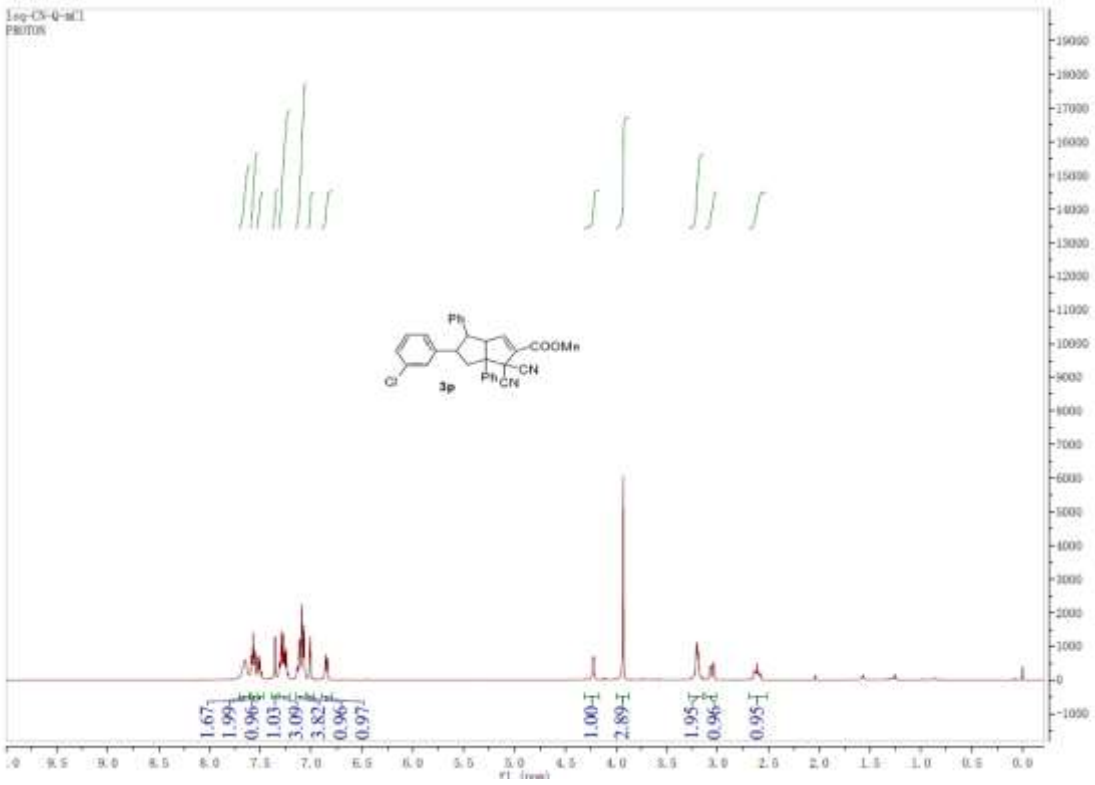
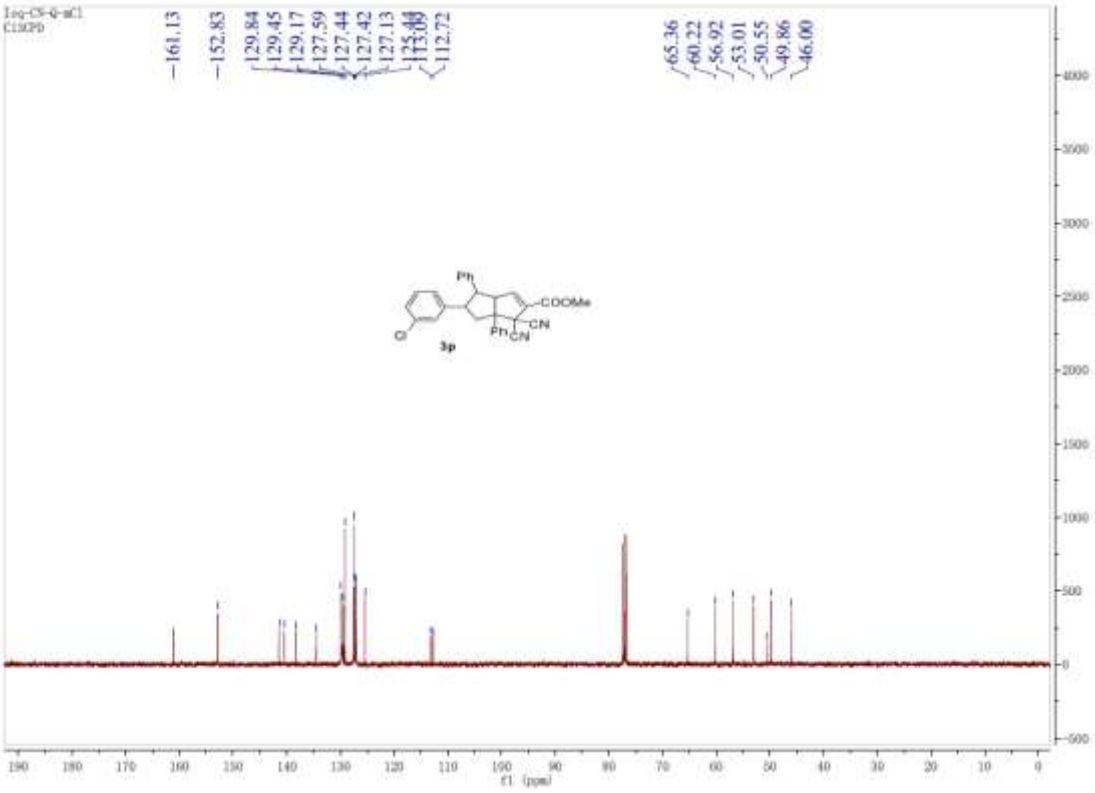
2.17
1.11
1.06
3.24
2.48
0.87
1.05
1.10
1.01
1.05
3.00
2.04
1.02
1.03
2.98


161.27
153.26
129.33
129.05
128.45
127.96
127.73
127.54
127.35
114.26
113.25
112.90
77.46
77.14
76.83
65.44
60.40
56.77
53.00
50.57
50.07
46.39
21.43
Ph
COOMe
CN
CN
3o


Ph
COOMe
Cl
CN
Ph
CN
3p
1.67
1.99
0.96
1.03
3.09
3.82
0.96
0.97
1.00
2.89
1.95
0.96
0.95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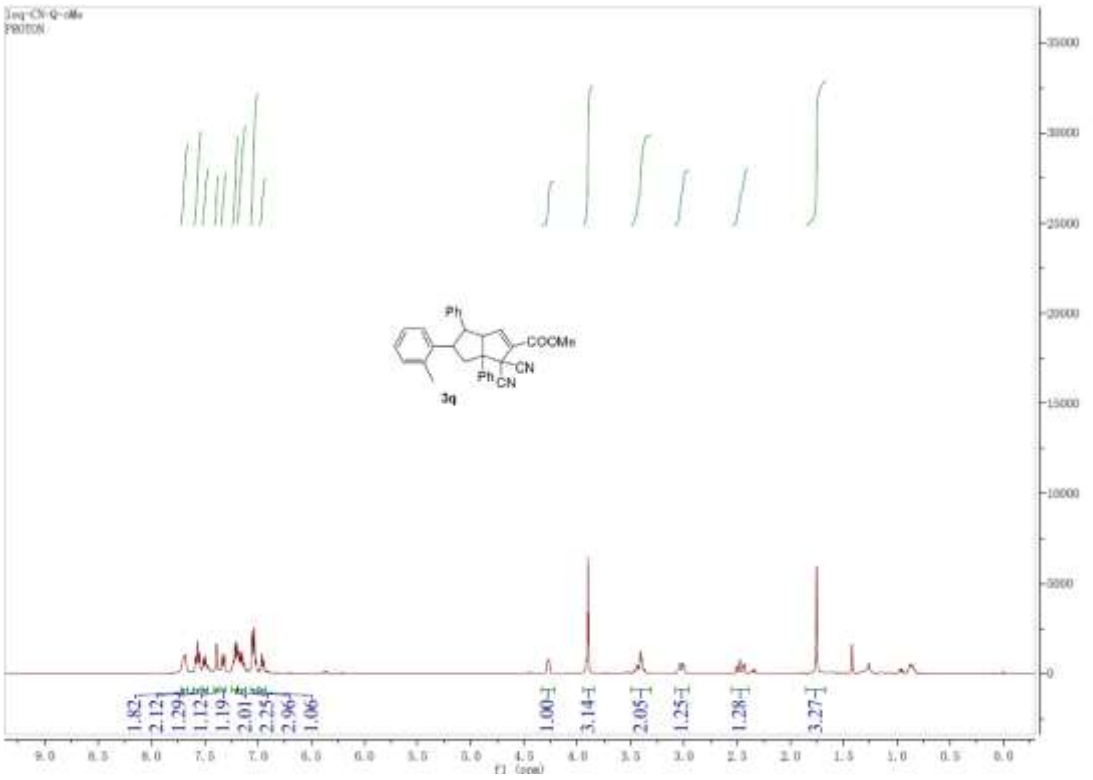
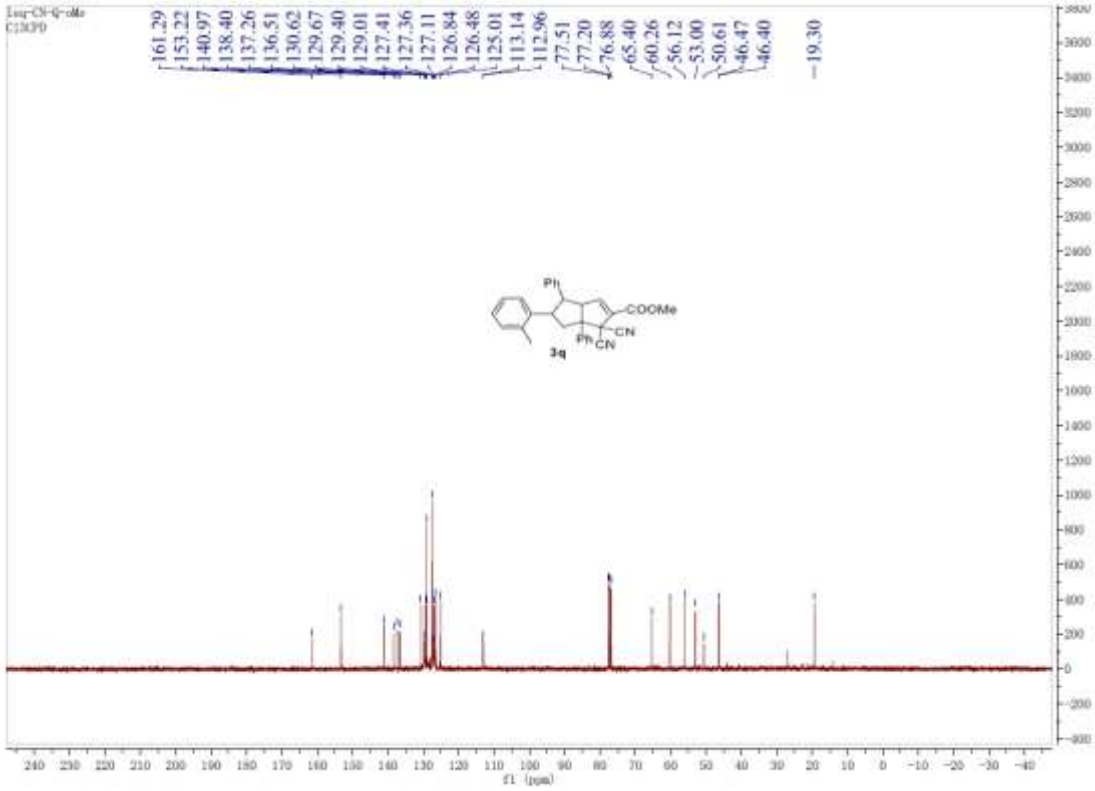
152.83
129.84
129.45
129.17
127.59
127.44
127.42
127.13
112.72
65.36
60.22
56.92
53.01
50.55
49.86
46.00
Ph
COOMe
Cl
CN
Ph
CN
3p


Ph
COOMe
CN
Ph
CN
3q
1.82
2.12
1.29
1.12
1.19
2.01
2.25
2.96
1.06
1.00
3.14
2.05
1.25
1.28
3.27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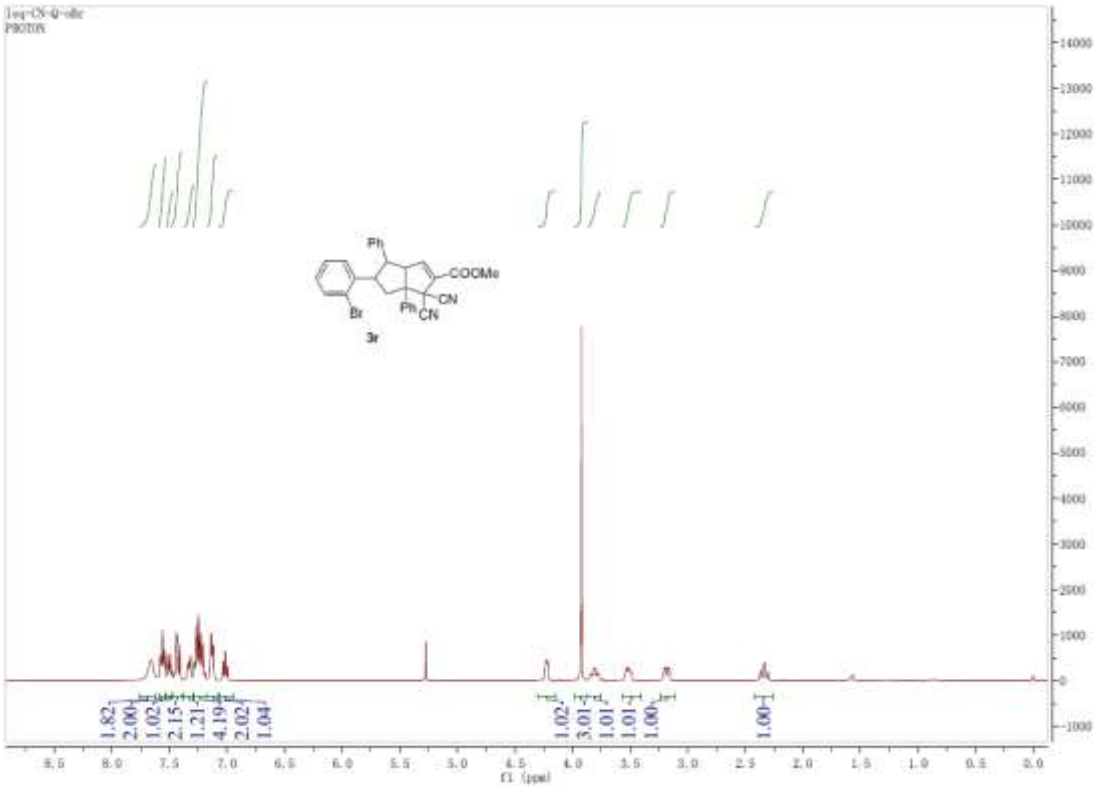
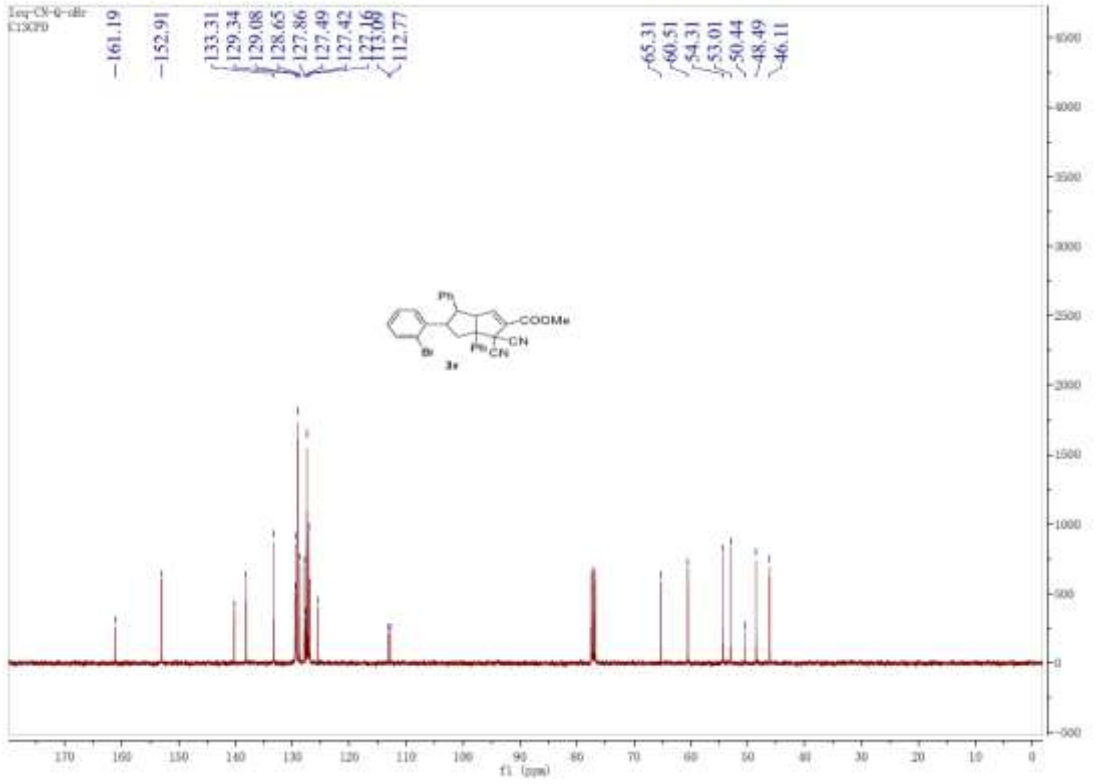
140.97
138.40
137.26
136.51
130.62
129.67
129.40
129.01
127.41
127.36
127.11
126.84
126.48
125.01
113.14
112.96
77.51
77.20
76.88
65.40
60.26
56.12
53.00
50.61
46.47
46.40
19.30
Ph
COOMe
CN
Ph
CN
3q


Ph
COOMe
CN
Ph
CN
Br
3r
1.82
2.00
1.02
2.15
1.21
4.19
2.02
1.04
1.02
3.01
1.01
1.01
1.00
1.00
f1 (ppm)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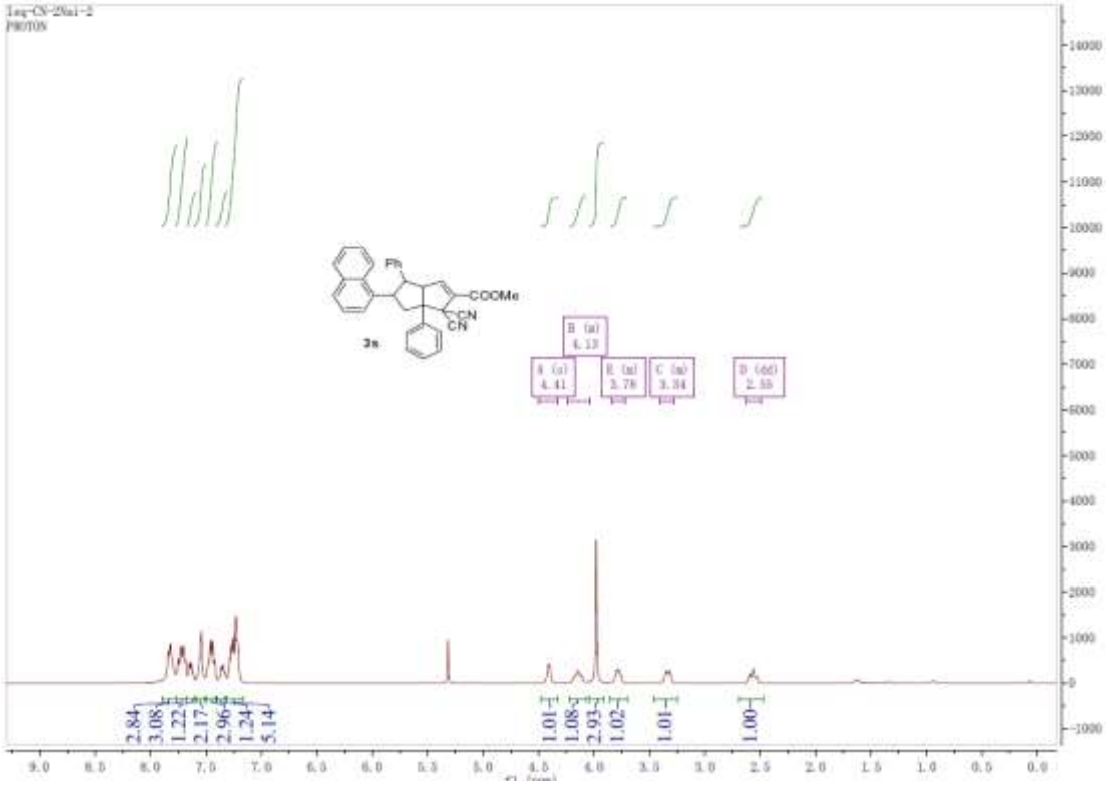
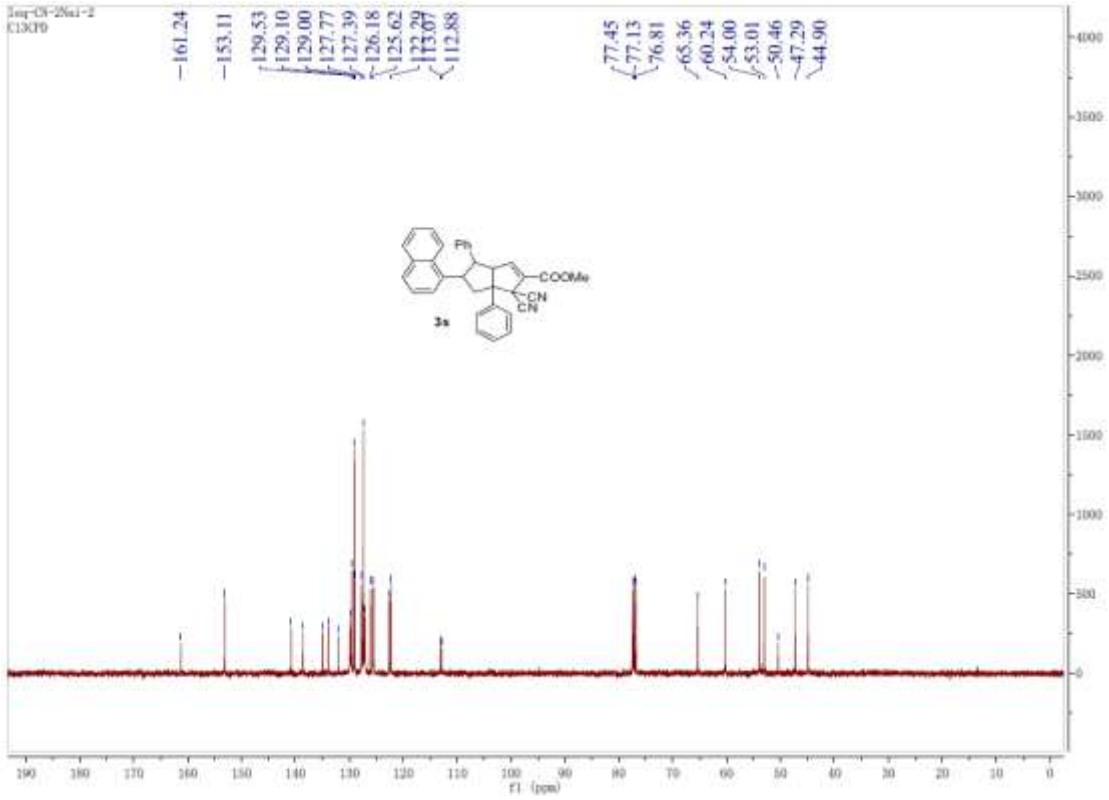
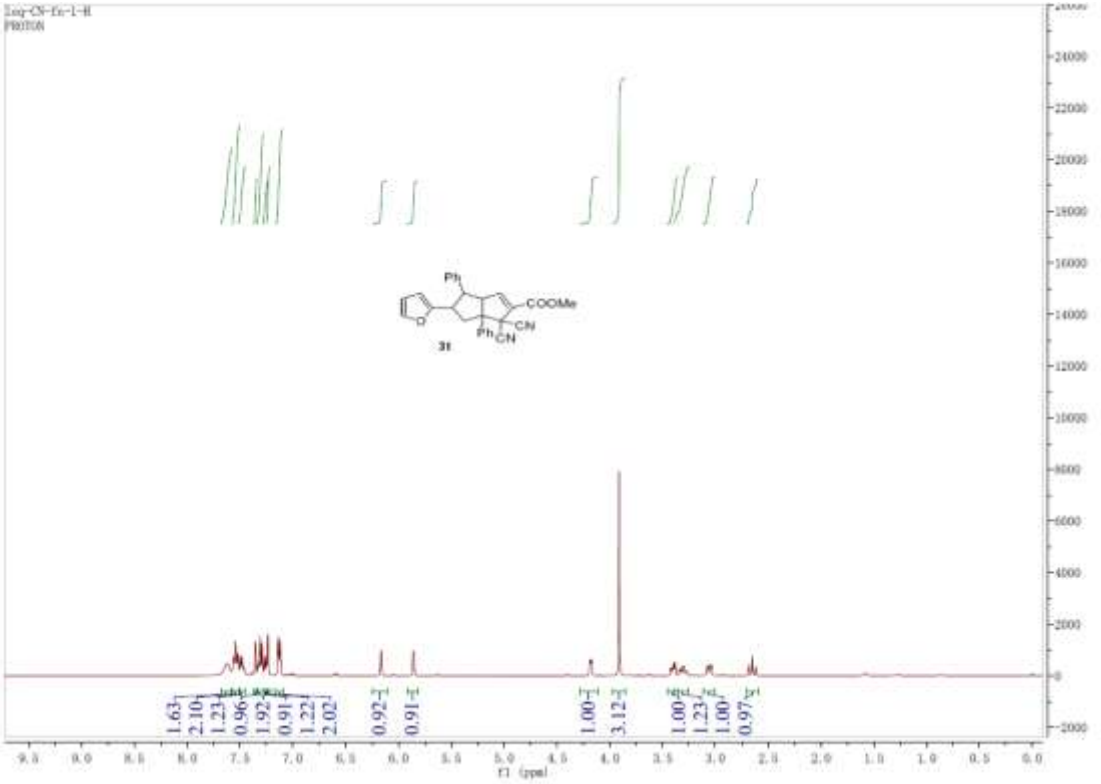
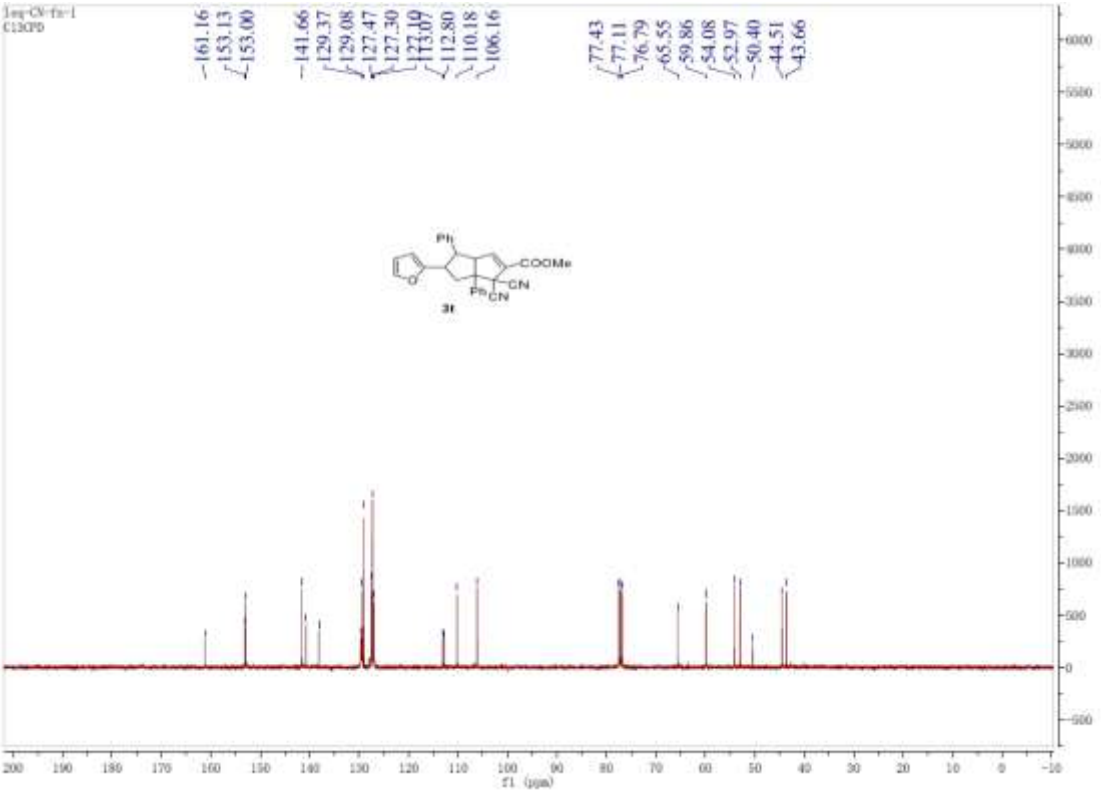
152.91
133.31
129.34
129.08
128.65
127.86
127.49
127.42
127.16
113.09
112.77
65.31
60.51
54.31
53.01
50.44
48.49
46.11
Ph
COOMe
CN
Ph
CN
Br
3r
f1 (ppm)


Ph
COOMe
CN
CN
3s
2.84
3.08
1.22
2.17
2.96
1.24
5.14
1.01
1.08
2.93
1.02
1.01
1.00


161.24
153.11
129.53
129.10
129.00
127.77
127.39
126.18
125.62
122.29
113.07
112.88
77.45
77.13
76.81
65.36
60.24
54.00
53.01
50.46
47.29
44.90
Ph
COOMe
CN
CN
3s


Ph
COOMe
CN
Ph
CN
3t
1.63
2.10
1.23
0.96
1.92
0.91
1.22
2.02
0.92
0.91
1.00
3.12
1.00
1.23
1.00
0.97
f1 (ppm)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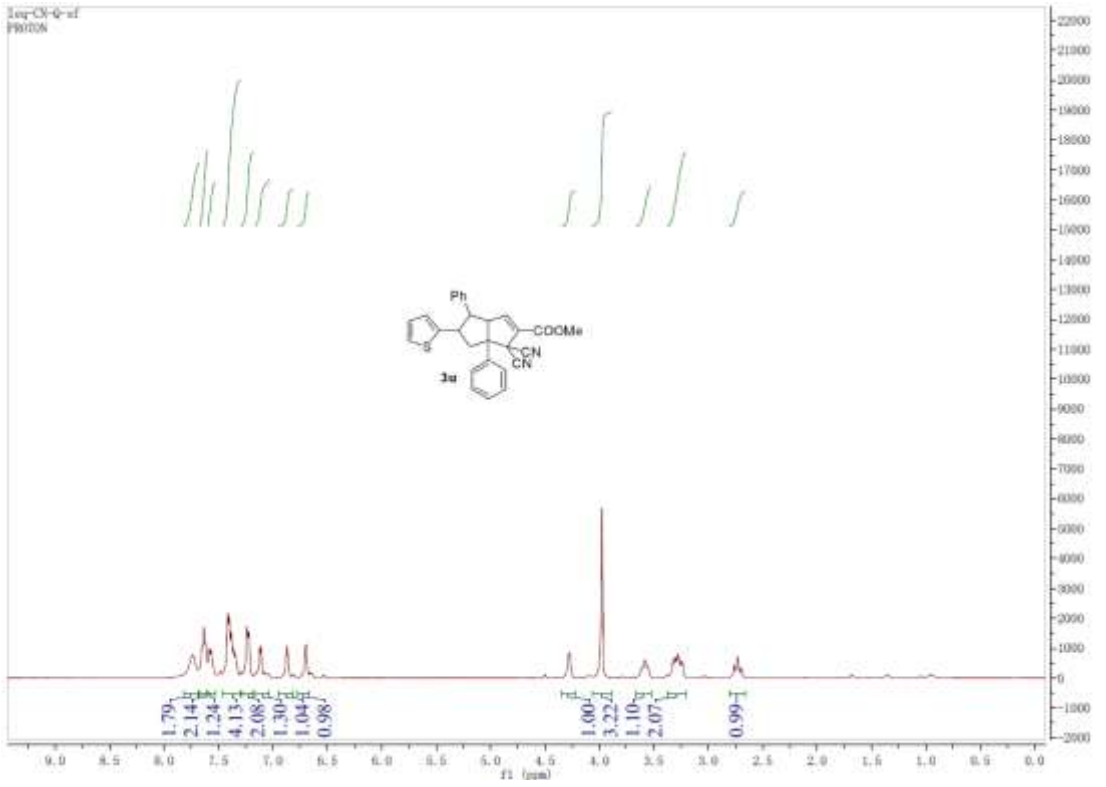
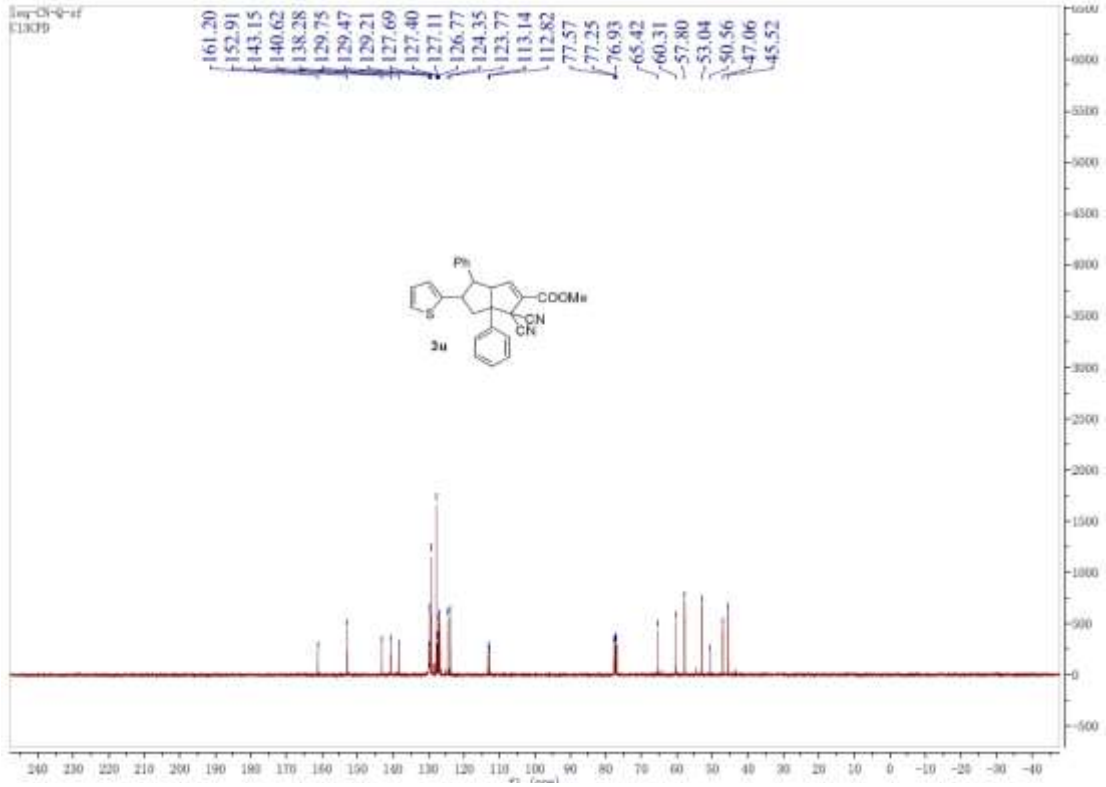
153.13
153.00
141.66
129.37
129.08
127.47
127.30
127.10
113.07
112.80
110.18
106.16
77.43
77.11
76.79
65.55
59.86
54.08
52.97
50.40
44.51
43.66
Ph
COOMe
CN
Ph
CN
3t
f1 (ppm)


Ph
COOMe
CN
CN
3u
1.79
2.14
1.24
4.13
2.08
1.30
1.04
0.98
1.00
3.22
1.10
2.07
0.99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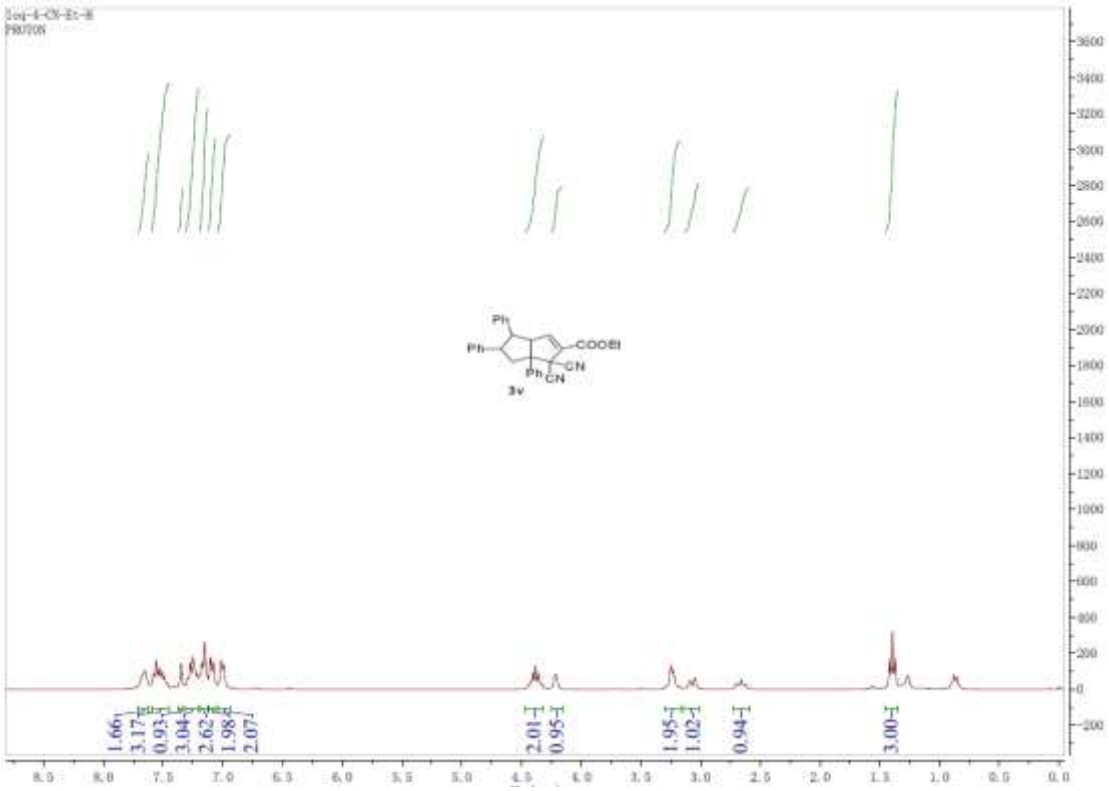
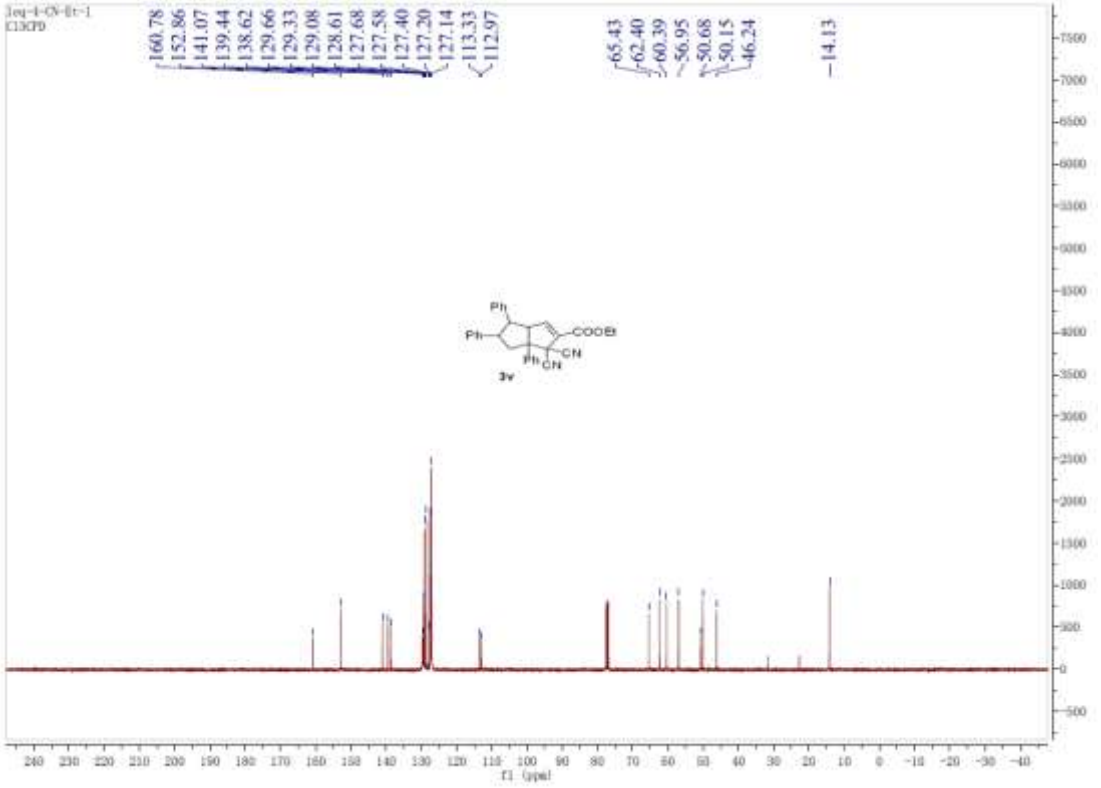
152.91
143.15
140.62
138.28
129.75
129.47
129.21
127.69
127.40
127.11
126.77
124.35
123.77
113.14
112.82
77.57
77.25
76.93
65.42
60.31
57.80
53.04
50.56
47.06
45.52
Ph
COOMe
CN
CN
3u


1.66
3.17
0.93
3.04
2.62
1.98
2.07
2.01
0.95
1.95
1.02
0.94
3.00
COOEt
CN
Ph
3v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141.07
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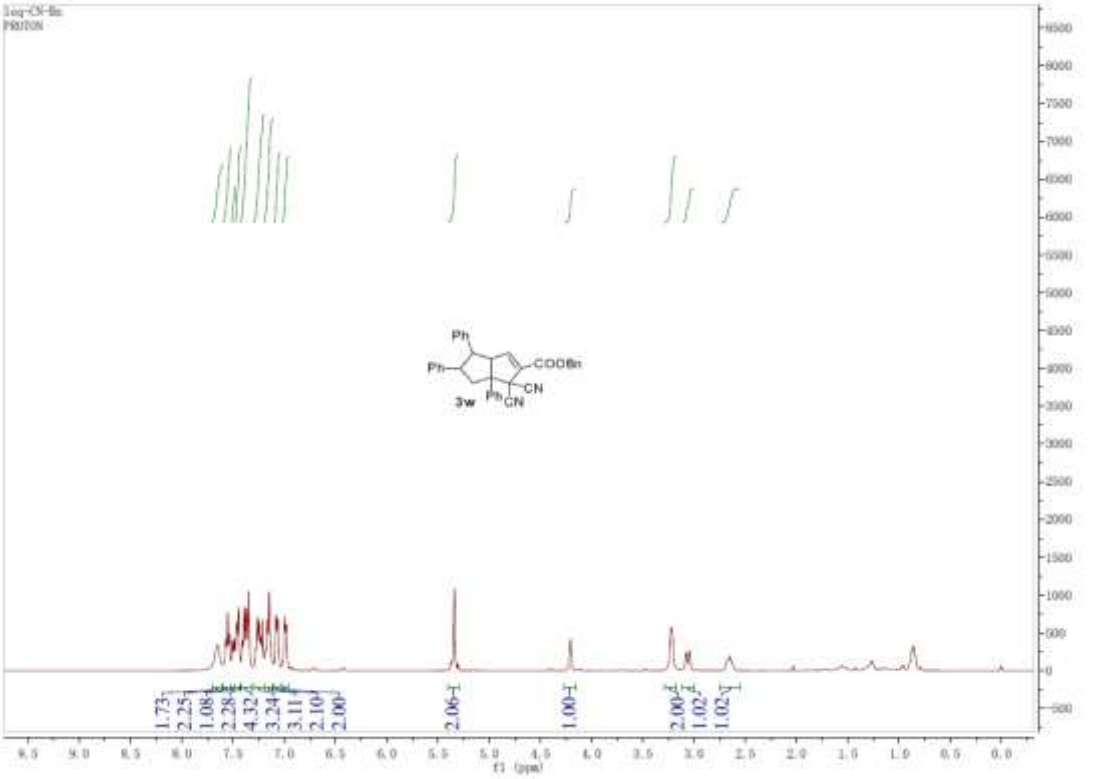
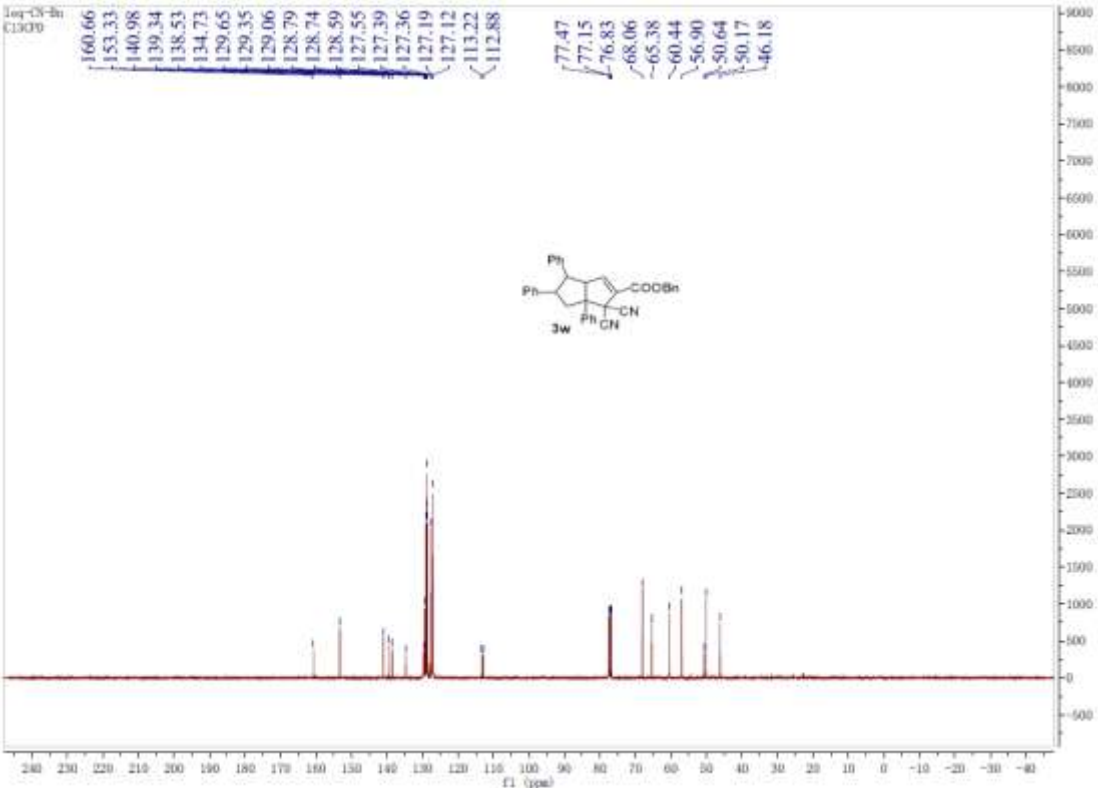
129.66
129.33
129.08
128.61
127.68
127.58
127.40
127.20
127.14
113.33
112.97
65.43
62.40
60.39
56.95
50.68
50.15
46.24
14.13
COOEt
CN
Ph
3v


Ph
Ph
COOBn
CN
Ph
CN
3w
1.73
2.25
1.08
2.28
4.32
3.24
3.11
2.10
2.00
2.06
1.00
2.00
1.02
1.02
f1 (ppm)


160.66
153.33
140.98
139.34
138.53
134.73
129.65
129.35
129.06
128.79
128.74
128.59
127.55
127.39
127.36
127.19
127.12
113.22
112.88
77.47
77.15
76.83
68.06
65.38
60.44
56.90
50.64
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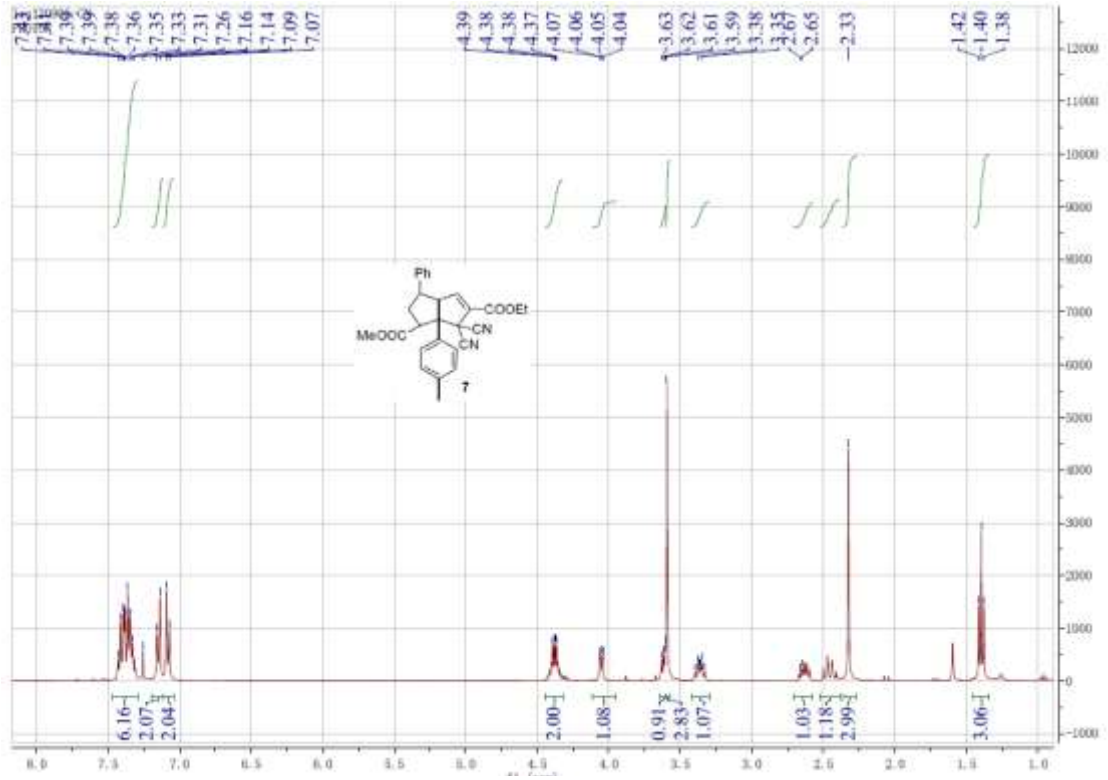
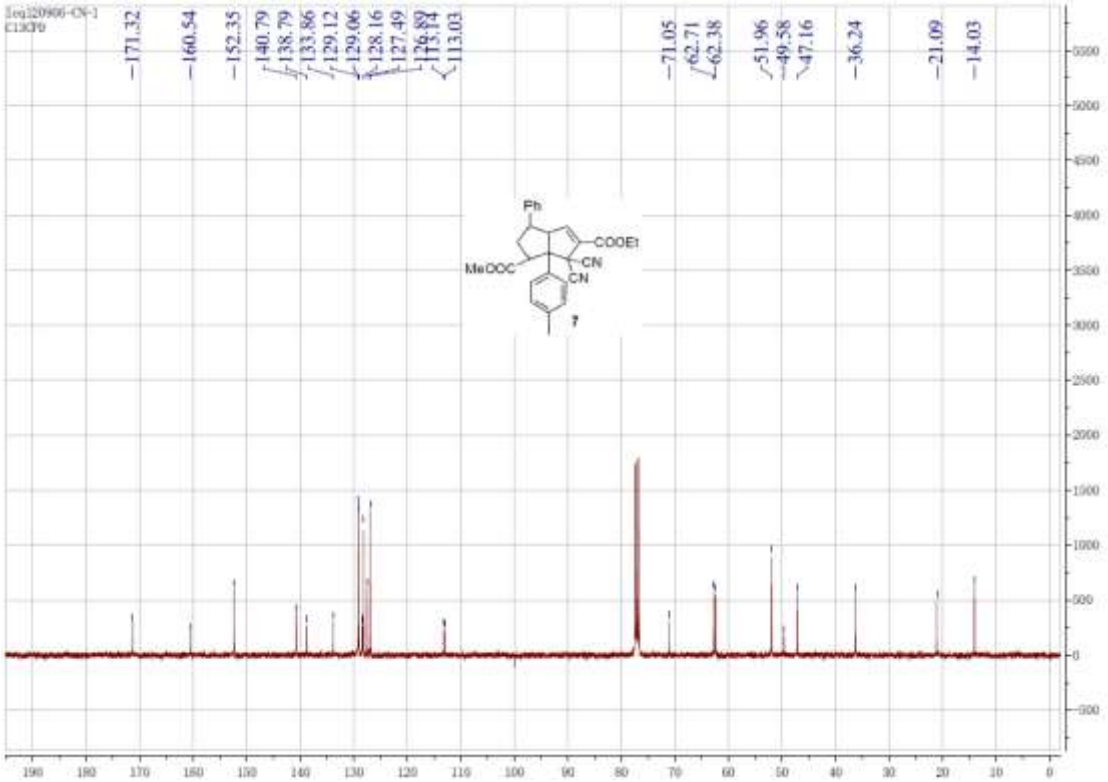
Ph
Ph
COOBn
CN
Ph
CN
3w
f1 (ppm)


Ph
COOEt
MeOOC
CN
CN
7


Ph
COOEt
MeOOC
CN
CN
7

VIII. single-crystal X-ray analysis 3a.